GASOLINE

AND

OTHER MOTOR FUELS

BY

CARLETON ELLIS

CONSULTING CHEMIST

Author of "Hydrogenation of Oils, Catalyzers and Catalysis, and the
Generation of Hydrogen and Oxygen"

MEMBER OF AMER ASSOC FOR THE ADVANCEMENT OF SCIENCE, AMER CHEM SOC; AMER ELEC-
TROCHEM SOC, AMER INST OF CHEM ENGRS, AMER MICROSCOPICAL SOC, AMER
OIL CHEMISTS SOC, FRANKLIN INSTITUTE, INVENTORS' GUILD, SOC OF CHEM
INDUS, SOCIÉTÉ DE CHIMIE INDUSTRIELLE, FELLOW OF THE CHEM
SOC, PRESIDENT NEW JERSEY CHEMICAL SOCIETY

AND

JOSEPH V. MEIGS

RESEARCH AND CONSULTING CHEMIST

Chief Chemist Massachusetts Oil Refining Company

MEMBER AMER CHEM SOC, AMER ASSOC FOR THE ADVANCEMENT OF SCIENCE SOC OF CHEM
INDUSTRY, SOCIÉTÉ DE CHIMIE INDUSTRIELLE FRANKLIN INSTITUTE,
NEW JERSEY CHEM SOC

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is therefore relatively small, as follows naturally when it is considered that the raw material used is a selected distillate. If it were possible to employ as raw material a wide fraction of the crude oil, for example, reduced asphaltic crudes which are used for the production of road oils and asphalt, and to convert about 25 per cent of such residues smoothly into gasoline, our supplies of the latter necessity would obviously be greatly increased.

This is doubtless one of the many reasons for the never ending supply of "new" cracking processes which appear in the literature at a steady and ever increasing rate.

Roughly speaking, 75 per cent of our gasoline is still represented by that which is naturally contained in the crude oil, about 10 per cent coming from natural and casing head gas and approximately 15 per cent being comprised of cracked gasoline.

The application of cracking methods to as wide a fraction or to as large a portion as possible of the crude oil therefore remains an incentive to attain a goal toward which further development tends.

The question "What is gasoline?" is one to which considerable time and argument may be given. In the refinery the term gasoline is not heard so frequently as the expression naphtha. Finished gasoline is what the refiner has in mind as the product obtained when portions of naphtha distillate have been submitted to purification by chemical treatment (or otherwise) and steam distilled. Similarly kerosene is a product made by purifying burning oil.

The sources of what we now call gasoline are so many and the actual composition of the product so variable, that it is somewhat difficult to give an adequate definition without begging the question. For example, if we state that "gasoline is a mixture of petroleum hydrocarbons having such properties that the mixture may be successfully employed as fuel for an internal combustion engine of the low-compression type i.e. the type now used in automobiles," we are at once defining gasoline in terms of its function in connection with the internal combustion engine. It is not difficult to define certain kinds of gasoline but another matter to find a definition that includes all the varieties and is at the same time not vague or functional.

In England "petrol" is the term commonly used to designate what we call gasoline in the United States. On the Continent benzine is a term often employed for the purpose especially in refineries. Essence is frequently applied to designate motor fuel in France.

The authors have classified the various methods of converting high boiling hydrocarbons into lower boiling ones according to a system which is conceded to be arbitrary, and have used their judgment as

to whether a given method should properly be placed in this or that category. The exercise of judgment of this nature is not without its difficulties and is by no means infallible. Neither is this classification a permanent one. As the art advances, methods undergo change. Some become obsolete, others experience development and adaptation which brings their previous classification into question. And, since in many cases advancement in principle and detail is very rapid, a classification which is justified today may be seriously questioned six months hence. The present classification is therefore submitted, with its limitations and with the request that suggestions for improvement be forwarded to the authors.

Although new oil fields are constantly being developed in the United States as well as in Mexico, South America and other countries, nevertheless the time has arrived when sources of motor fuel other than petroleum must be given serious consideration, active research and commercial exploitation. Chief among these other sources are alcohol and shale oil, with the products of distillation of coals, lignites, asphalt and peat following. This is the order of importance which the authors consider to be correct for the United States, although some may wish to place shale oil first. Further development in the low temperature distillation of coal or other suitable treatment of coal may also change its position as regards its relative importance as a source of motor fuel for automobiles.

Alcohol has repeatedly been advocated as a motor fuel both singly and also when admixed with benzol and other hydrocarbons. Since sugar is looked upon as the most universal source of raw material for the manufacture of alcohol many countries deficient in petroleum have been investigating their sugar resources. Commissions appointed by various governments have of late been carefully studying the situation with respect to the production of sugar. The direct fermentation of wood fiber or cellulose to make alcohol is a problem on which work has been done and the solution of such a problem would appear to solve the motor fuel requirements for a number of countries deficient in natural petroleum.

Benzol, the volatile spirit of coal tar, is also an excellent motor fuel and is being used extensively at the present time usually in admixture with gasoline. It has excellent propelling power, but the supply is not great in comparison with gasoline.

Considerable attention is being given to the adaptation of heavy oils, such as kerosene, for use in present types of motors. This is a very important and interesting subject and the successful solution of the problem, which requires both engineer and chemist, means increas-

PREFACE

The field of motor fuel has become so enormous that a special treatise on this subject appeared to be warranted. The authors have endeavored to bring together in this volume such material as would constitute a substantially complete survey of this field. An endeavor of this description has not been without its labors and while shortcomings undoubtedly will be discovered in its pages it is believed the book will be found to afford a description of practically every process of making gasoline and of most other motor fuels of promise and prominence.

Since motor fuels have secured so strong a foothold in the everyday affairs of mankind there has been the most remarkable activity among inventors and engineers to improve the methods of making gasoline and to utilize kerosene, benzol, alcohol and the like as well as to contrive the production of entirely new liquid fuels. As a result thousands of patents have issued. The authors' survey of these patents has, it is hoped, been adequate to meet the requirements of the numerous investigators now concerned with the manifold phases of this field. It is the expectation of the authors that the volume will be found to contain very many suggestions to the practical operator for the improvement of plant methods. Effort has been made to strike a balance between the theoretical and the practical in the description of this industry. For the inventor and patent attorney the volume should be of considerable service; and the business man or banker who is interested in developing or promoting some one of the many methods advanced for the production of motor fuel, will find the book of easy reference owing to the complete index which is appended.

The criticism may be advanced by some that the inclusion of so large a number of processes described only in the patent literature is undesirable as it tends to encumber the pages with what they might term to be useless material. The authors have already given this consideration careful thought and in doing so reached the conclusion that a complete survey of the art was better than a fragmentary discussion. Such a decision was reached after observing how certain methods which were advocated years ago and at that time were held up to derision are now in operation on the large scale. Systems which

looked entirely impracticable a few years ago, today are regarded as
vital in the industry. In the domain of motor fuels one improvement
has quickly followed another and it is of interest to observe this deriva-
tion, and to note the correlation of ideas. This treatise proposes to
show such derivation of different processes as far as possible.

It is perhaps a superfluity to add that the greatest source of motor
fuel is gasoline, partly naturally derived by a simple distillation of
crude petroleum and partly derived by the heat decomposition of
heavy oils or the so-called cracking processes, the number of which is
legion. The possibility of converting low-grade petroleum residues
into gasoline by the cracking method has called for inventive effort
of the most marked ingenuity, and more than twenty chapters of the
volume are devoted to the description of cracking processes as these
undoubtedly will be foremost in the ways and means of producing motor
fuel for many years to come. A substantial amount of gasoline is
recovered from natural gas and casing head naphtha has become a
well known product to refiners and blenders of motor fuels. Shale
oil is coming into prominence in this country and abroad.

In the following chapters will be found a consideration of our reserve
supplies of motor fuel, methods of preparation of typical fuels, such as
benzol and alcohol, as well as a discussion of the relative merits of such
materials as compared to those possessed by gasoline.

The substances enumerated above, viz. alcohol, shale naphtha,
benzol, toluol, etc., and the light oils distilled from asphalts, inferior
coals, lignite and peat are, singly or suitably blended, illustrations of
real "substitutes" for gasoline, as distinguished from certain mix-
tures, the actual merit of which often falls short of the claims made
by promoters and advertising agents. These mixtures frequently
contain a heavy oil mixed with a very volatile substance. Sometimes
they constitute a satisfactory motor fuel, but in many cases it is doubt-
ful whether any actual economy results from their use, although this
is frequently a question of local conditions. The authors consider
that every encouragement should be given to research directed toward
the increase in our fuel reserve and supply by the intelligent and scien-
tific blending of fuels from different sources and of different properties.
Consideration to this matter is given in Chapter I, and elsewhere
throughout the treatise.

The subject of motor fuel testing might well occupy a volume by
itself. Most motorists are interested to know how many "miles per
gallon" they obtain with their car. By using a good grade of blended
benzol, such as is obtained from some of the public utilities companies,
and comparing mileage under similar conditions with that obtained

with "straight" gasoline, the motorist may secure data for estimating
the efficiency of benzol as fuel. Information of this sort is obtained in a
manner that is more accurate and convenient, by the use of a dyna-
mometer. This instrument, properly manipulated, is the "court of
last resort" when comparing relative fuel efficiencies.

It is hoped that chapter 2, which discusses the question of the test-
ing of motor fuels, will be sufficiently informative to prove valuable
to those whose interest is directed toward this phase of the subject.

In conclusion, the authors desire to express their thanks to all who
have contributed their effort and criticism, including Mr. Joseph Tracy,
Mr. Frank A. Howard of the Standard Oil Company, Mr. F. N. Williams
of the Massachusetts Oil Refining Company, Mr. D. J. Collins of the
United Gas Improvement Company, Dr. Gustav Egloff of the Universal
Oil Products Company, Messrs. Moore, Toomey and Morrell, formerly
associated with Dr. Egloff at Columbia University, Dr. A. M. McAfee
of the Gulf Refining Company, and others.

It is also desired to acknowledge free use of the publications of the
United States Bureau of Mines and United States Geological Survey,
the excellence of which it is needless to state.

The authors likewise wish to acknowledge their use of the profes-
sional literature and to express their indebtedness and also their con-
gratulations to the host of workers whose untiring efforts have placed
the science and art of motor fuel manufacture in the advanced position
where it is found today.

It is the desire of the authors to make this volume as comprehensive
a treatise on gasoline and other volatile motor fuels as is possible to
compass in the space alloted and to this end any omissions, criticisms
and suggestions which the reader may offer will be gratefully acknowl-
edged. The authors especially would like to receive from those en-
gaged in development work, such descriptive matter and data as would
be useful in the preparation of subsequent editions of this volume.

ELLIS LABORATORIES,
98 Greenwood Ave.,   CARLETON ELLIS
MONTCLAIR, N. J.

33 Clinton Street,   JOSEPH V. MEIGS
MALDEN, MASS.

December, 1920

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INTRODUCTION

Many of the readers of this volume will readily recall the days when gasoline found practically no commercial outlet and was looked upon as a by-product and nuisance of the oil refinery. The stationary gas engine did but little to increase the market. The advent of the automobile, however, suddenly changed the situation. Gasoline became the chief instead of the by-product. Refineries were reconstructed to operate to produce the maximum of gasoline and other products often were considered of a subsidiary nature.

The demand for gasoline or equivalent motor fuel now comes from every department of our economic and industrial life as a nation, as well as from the corresponding phases of the activities of other nations and principalities. Farmers require gasoline to plant and harvest their crops. Railroad transportation facilities are not adequate and, in many cases, not sufficiently flexible, to keep pace with the intercourse between towns and municipalities, or to satisfy the modern passion for recreation as completely as this is accomplished through the medium of the pleasure automobile. Six hundred and fifty per cent is the figure that measures the increase in demand for crude petroleum in the last few years; while production in the same period of time has increased only 150 per cent. A registration of over 10,000,000 motor vehicles in the United States alone is conservatively estimated for the first of January, 1922. With the present relative balance between crude oil production and consumption, it has been estimated by some authorities that the oil fields of the United States will be exhausted by 1935. From oil wells by present methods only a small part, probably not more than 10 to 20 per cent, of the oil deposit is withdrawn. Oil is tenaciously retained in the microscopic pores of sandstone and other formations in a manner which has been likened to water held in a sponge. As one of the first considerations in insuring a future supply of gasoline Manning advocates technical and scientific investigations under government auspices, directed toward the winning of the 80 or 90 per cent of oil now locked in porous strata.

The method of increasing the supply of gasoline, commonly known as the cracking process, consists in converting a portion of heavy petroleum distillates into lighter oils by the application of some form of

energy, usually heat. An examination of many of the processes proposed for accomplishing this conversion might lead the layman to believe that it would be readily feasible to remove naphtha from crude petroleum and to convert the remaining residue into naphtha by the application of a cracking process. There are several reasons why this is not done at the present time.

First, it is usually desirable whenever commercially practicable to recover lubricating oils and wax, which in themselves possess values greater than could be realized, in general, by a conversion operation directed solely to the production of gasoline. This necessitates protecting the lubricant fractions from any decomposition which might impair their value and precludes the application of cracking to those residues containing the desired lubricants.

Secondly, to convert any residue or distillate boiling above the range of temperatures commonly connected with the properties of finished gasoline, quantitatively into lower boiling hydrocarbons is theoretically and practically impossible. In practice a certain amount of gas and coke (or at least oils possessing carbon contents greater than that of the oils selected for cracking) are always formed. Theoretically it is impossible to convert, quantitatively, a higher boiling saturated hydrocarbon into a lower boiling one, similarly saturated, unless extraneous hydrogen, in some form, is caused to enter into the decomposition reaction.

Although the recovery of lubricants and wax in many cases militates against the attempt to crack, in their entirety, oils from which naphtha and burning oil have been removed, nevertheless there are cases where such a procedure might be economically carried out, if a suitable process were available for carrying it into effect.

At the present time, a process is not known to the authors for executing this plan commercially and economically. The deposition of coke and other difficulties inherent in the evolution of a method for accomplishing this purpose do not as yet appear to have been surmounted, in spite of the host of cracking processes that have been proposed. There are probably methods which will accomplish the desired ends, in whole or in part, but they do not appear at present to have been brought to large scale development, as is evidenced in part by the fact that only about 15 per cent of the gasoline now annually consumed in the United States is obtained by cracking methods.

The raw material very largely used today for the production of cracked gasoline is gas oil, the yield of which may be from 10 to 40 per cent of the entire crude. This yields, say 25 per cent of gasoline by cracking. The amount of gasoline produced by cracking processes

ing greatly our fuel supply. The question is partly one of engine design, partly one of finding a suitable commercial blend.

There is a vast difference between the scientific blending of fuels and the production of mixtures made merely to sell.

Attention is called to the numerous proposals which appear from time to time in the press for making motor fuel from some inconceivably cheap material. These, when investigated carefully, generally prove to be mixtures of various volatile combustible materials many of which are considerably more expensive than gasoline. It is time that light should be thrown on compositions of this character which are heralded by the press in many instances as representing discoveries of wonderful value but which in point of fact are not based on sound chemical or economic principles. Money should not be frittered away in exploiting fuels which have no proper fundamental right of existence, and the present volume endeavors to make clear in what fields and along what routes the motor fuel industry may be preserved and carried out to best advantage.

MOTOR FUELS

CHAPTER I

MIXED FUELS

ᵃ It is possible to operate an internal combustion engine requiring a volatile or relatively volatile fuel, for example the automobile motor, with any combustible fluid provided the latter possesses (a) the ability to vaporize with sufficient rapidity, (b) the property of exploding when its vapor is mixed with air and provided that the pressure developed by the explosion or inflammation of the air-vapor mixture is sufficient to do the work necessary. This naturally permits wide latitude in the choice of pure substances or mixtures intended for use as motor fuel. The average fuel cost per brake horsepower developed per hour, operating properties such as smooth running at various speeds and under varied climatic and seasonal conditions, ease of starting from " all cold," rapid accelerating ability, the nature and properties of the products of combustion (complete and incomplete), the effect of those products on the cylinder and other engine parts, the available supply of the fuel from year to year — these and other standards place practical limits on the choice of raw material.

As classes of raw materials to choose from there are first the hydro-carbons. These may be divided into two general types: (a) petroleum hydrocarbons including the paraffins, olefins and acetylenes, the alicyclic and naphthene hydrocarbons and (b) aromatic hydrocarbons. Secondly, there are the compounds containing oxygen in addition to carbon and hydrogen, including the alcohols and ethers. A third and miscellaneous class includes substances such as carbon monoxide, carbon bisulphide, and the elements carbon and hydrogen.

A thorough examination will disclose the fact that investigators have drawn heavily upon members of the family groups enumerated in the endeavor to increase the present and future supply of available motor fuel.

One of the main ideas has been to make a fuel which is composed of more than one type of substance, for example alcohol and benzol,

or benzol and gasoline, or alcohol, benzol and gasoline, gases dissolved
in liquids (e.g. acetylene in acetone, illuminating gas in benzol, olefinic
gases in alcohol) or solids dissolved in liquids (e.g. naphthalene in
benzol). These proposals are fundamentally correct since they con-
template drawing upon as many of our natural resources as possible,
with a view to avoiding the depletion of any one of those resources.

Again, the inability of the present type of gasoline engine to burn
heavy fuels has led to research which will modify those heavy fuels so
that they will be as suitable for the purpose as gasoline. At the base
of this endeavor lies the phenomena of minimum boiling mixtures which,
stated briefly means that when certain liquids having relatively high
boiling points and mutually soluble in each other are combined in a state
of solution in the correct proportions, the mixture or solution possesses
a constant boiling point and one which is lower than that of any of the
bodies of which it is composed. The mixture may involve two or
more individual substances. There is a great deal of opportunity for
investigation for the purpose of lowering (in effect) the boiling points of
the heavy hydrocarbons (and higher alcohols) by determining mixtures,
containing these substances, which possess comparatively low and
constant boiling points.

In the attempt to utilize the comparatively high boiling oils, some
investigators have endeavored to contribute volatile properties to these
substances by dissolving gases in the oils. Such solutions, however,
cannot hope to meet with much success, in general, particularly where
the oil is of the more nonvolatile variety. Other proposals go still
further and attempt to force the issue by employing such substances
as picric acid, ammonium nitrate, etc. Except in special cases, the
latter idea does not appear to possess much genuine merit.

It would appear that the economic necessity for "mixed" volatile
fuels will continue to grow, for some time, in view of the increase in
the production of motors for automobiles, aeroplanes, and other pur-
poses and considering that the production of petroleum, at least in the
United States, is expected to reach a maximum in a few years.[1]

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[1] Appropriation of $250,000 for the use of the Bureau of Chemistry in the dis-
covery of a substitute for gasoline is called for in a bill introduced in the House by
Representative Harold Knutson of Minnesota (Chemical Age, New York, Vol. 28,
1920, p. 189).

"In view of the threatened shortage of gasoline," said Mr. Knutson, "I have
been moved to prepare and introduce the resolution which follows below. In the
three years that I have been in Congress I have given this subject considerable
study. My first plan was to take off all restrictions on the manufacture of denatured
alcohol, but it was thought by many members of Congress that this would result
in a large number of illicit stills springing up over the country, and in deference to

J. H. Hunt [1] classifies the difficulties encountered in the use of fuels heavier than gasoline as follows: Starting, carburetion, distribution and combustion. Bringing the temperature of all parts of the carburetor, inlet manifold and cylinder walls to the final operating temperature by means of special heating devices before cranking, or at least before using a heavy fuel, is advised. The practice of " choking " in starting, that is, supplying an excessive amount of fuel, of which only a small amount is vaporized, to form an explosive mixture, leads, it is stated, either to tarry deposits in the cylinder, or often to leakage past the piston rings into the lubricating oil in the crank case.

Butterfield [2] considers that a matter which calls for further investigation is the relative bearing of different physical properties of the several constituents of motor spirit on ease of starting an internal combustion engine when cold. It is well known that of two different brands of gasoline, both giving practically the same distillation curve, one affords easy starting while the other presents great trouble in this respect, though once the engine is running there is nothing to choose between the two brands. Sometimes, indeed, the gasoline which is troublesome at starting is distinctly superior, if the engine becomes overheated, in respect to liability to pre-ignition. It is not certain on what characteristics of gasoline ease of starting depends, for though the vapor pressure at low temperatures and vapor density are undoubtedly of primary importance, it seems likely that the temperature of ignition plays a part here as it certainly does in determining the

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their views I have temporarily given up that plan for the one now called to your attention. This resolution I have introduced in the House.

Text of Bill: " Whereas, gasoline is a commodity of universal use and is indispensable in the agricultural and commercial progress of modern civilization, and the paramount importance of a sufficient supply of gasoline, or a suitable substitute therefor to supply the needs of the American people is a self-evident proposition; and

" Whereas, the reserve and visible supply of gasoline is being rapidly exhausted by the growing demand, and the price of which is being advanced to unprecedented levels; and

" Whereas, the existing scarcity of gasoline and its threatened total exhaustion in the United States has become a matter of such grave concern to the agricultural and commercial interests of the country that it becomes absolutely imperative that a substitute therefor be found: Therefore be it

" Resolved by the Senate and House of Representatives of the United States of America in congress assembled, that the sum of $250,000 be and is hereby appropriated to be used by the Bureau of Chemistry, Department of Agriculture, in discovering a suitable substitute for gasoline."

[1] J. Soc. Automotive Engineers, 1919, 202.

[2] Reports of Soc. Chem. Ind. 1917, II, 74.

liability to pre-ignition. The spontaneous ignition temperatures of liquid fuels have been investigated by **H. Moore,** especially, however, in regard to fuel oils suitable for use in Diesel engines.[1] His work, however, leads to the general conclusions, which are applicable to motor spirit also, that aromatic compounds have much higher ignition temperatures than aliphatic compounds, saturated compounds higher than unsaturated, and compounds containing simple molecules higher than similar compounds containing more complex molecules. These conclusions should be very helpful to compounders of " gasoline substitutes," whose empirical pioneer work should not be despised, since there is little question that in the near future the bulk of the motor spirit supplied will be prepared by blending materials of different origin, composition, and characteristics. Apart from the benefit to be derived from the utilization by this means of large quantities of materials unsuitable alone for use as motor spirit, it seems probable that a full knowledge of the properties and behavior of different series of hydrocarbons, etc., will lead to the preparation of motor spirits by blending which will be superior to any straight-run gasoline, when all essentials of a good motor spirit have been taken into account.

An unique suggestion for the production of a liquid fuel suitable for use in internal combustion engines comes from **J. M. O'Brien.**[2] Ordinary commercial paraffin is agitated with strong sulphuric acid, bleaching powder, and petroleum ether respectively. The filtered material may be mixed with gasoline in various proportions, and if desired may be treated, it is said, with silicic acid in an absorbent form.

The type of gasoline substitute which is of most importance at the present time is the mixture of hydrocarbons obtained as a by-product in the coking of coal, according to **E. W. Dean.**[3] These so-called coal tar distillates, including benzol, toluol, xylol, etc., are hydrocarbons which are somewhat similar to the hydrocarbons found in petroleum, although of course there are well-recognized physical and chemical differences. During the war, coal tar distillates were largely used in the production of explosives and other munitions, but since the termination of hostilities a considerable supply has been rendered available for motor fuel. Several companies have already undertaken to market benzol mixtures and in the course of its 1919 survey the U. S. Bureau of Mines secured a number of samples which were sold as gasoline substitutes containing benzol. The distillation curve of one of the samples is shown in Fig. 1 and of some of the other samples in Fig. 2. The products are generally mixtures of coal tar distillates with petroleum naphtha. These products have been used under

[1] J. S. C. I., 1917, 109.   [2] British Patent 111,864, Sept. 5, 1916.
                    [3] J. Frank. Institute, March, 1920.

widely varying conditions and in some cases favorable results have been obtained, in others unfavorable results. Inquiries made have usually been answered, according to Dean, by statements either that the substitutes were very satisfactory or very unsatisfactory, few of the users seeming to have found them about the same as petroleum gasoline.

The use of coal tar distillates as motor fuel does not, however, offer an ultimate solution of the motor fuel problem, as the total produc-
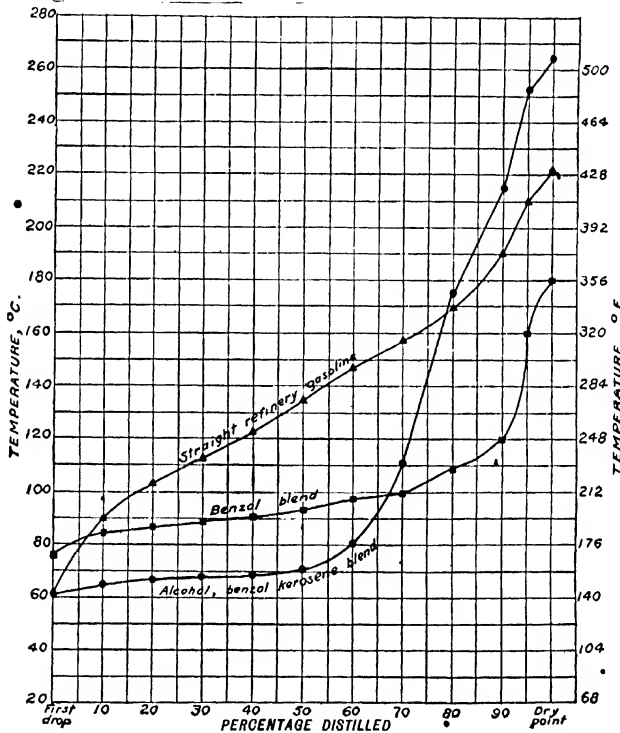
Fig. 1. — Showing distillation curves of three different types of motor fuel. (1) A blend of alcohol, benzol, and kerosene. (2) A blend containing benzol as principal constituent. (3) A straight refinery motor gasoline.

tion of these hydrocarbons is rather limited. In discussing this subject in a paper prepared several years ago Dean collected some statistics which are represented graphically in Fig. 3. This figure shows:

1. The nation's gasoline production in 1916.

2. An estimate of the total light oil production if all the bituminous coal mined in the country were coked in by-product ovens.

3. An estimate of the production of light oil, if all coking ovens were of the by-product type.

4. An estimate of the actual light oil production for the year 1917.

The actual figure for hydrocarbons suitable for motor fuel is even less than that for total light oil produced, and it appears, therefore, that as a motor fuel resource, coal tar distillates are of relatively small impor-
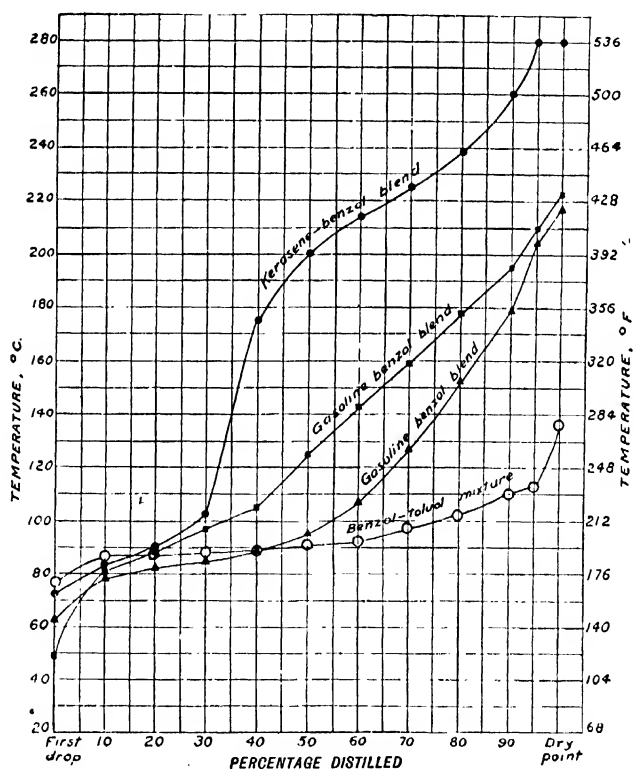
Fig. 2. — Showing distillation curves of four motor fuels containing coal-tar distillates.

tance. It may, for instance, be stated that since 1916 the production of gasoline has practically doubled while the quantity of coal mined has increased only about 17 per cent. The real importance of coal tar distillates as motor fuel occurs in districts adjacent to by-product coking operations where a reasonable proportion of the local gasoline supply may be filled by coal tar products.

Benzol and other coal tar distillates have certain disadvantages

when compared with petroleum gasoline but have other very marked advantages; particularly in freedom from tendency to knock. An additional advantage lies in the fact that they have a considerably higher calorific value per unit volume, and as this is the basis on which the user buys, he gets more for his money than he would from petroleum gasoline. It is believed that coal tar distillates, if properly used, are very satisfactory motor fuels and that there should be little difficulty in finding a market for the entire supply.

PRODUCTION	MILLION GALLONS					
	0	500	1000	1500	2000	2500
Gasoline production in 1916	////////////////////////////////					
Possible light oil production if all bituminous coal mined in 1916 were coked in by-product ovens	////////////					
Possible light oil production if all coking operations in 1916 were conducted in by-product ovens	//					
Maximum estimated light oil production for year 1917	/					
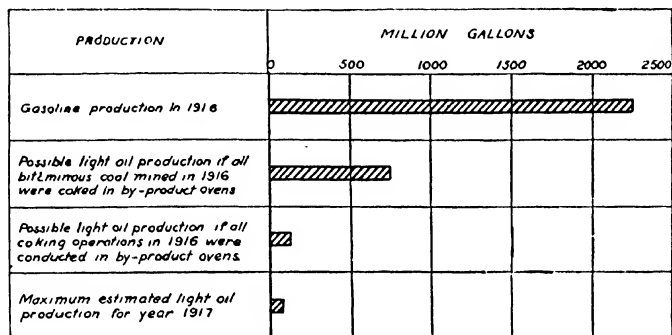
Fig. 3. — Showing the relative magnitude of petroleum gasoline production as compared with possible resources of coal-tar distillates.

J. A. Stoneham[1] suggests a fuel for internal combustion engines consisting of a mixture of benzol with derivatives of petroleum having a flash point above 120°F. (49°C.) and coal-tar distillates having a flash point between 80°F. and 90°F. (27°–32°C.). A small quantity of ether may be added to the mixture.

Crude wood naphtha mixed with kerosene is proposed as a motor fuel by **G. F. Dinsmore.**[2] The acetone in the wood naphtha is dissolved by the kerosene, and the solution is separated from the undissolved methyl alcohol.

Belisario Diaz Ossa[3] describes a fuel designed to make Chile independent of foreign petroleum and gasoline. It is called " E-H-A," the name being abbreviated from the words " eter-hidro-carburo-alcohól " (i.e., ether, hydrocarbon, alcohol). It was developed by **Letoinbe** and **Mauclere** in 1916–1917. and consists of alcohol, 65 per cent ether, 10 per cent light gas, benzine 25 per cent. It is stated to have properties analogous to those requisite for automobiles.

[1] Chem. Abs., 1918, 423; British Patent 110,132, July 10, 1917.
[2] J. S. C. I. 1920, 290 A; U. S. Patent 1,331,054, Feb. 17, 1920.
[3] Chem. Abs., 1919, 2271: Bol. soc formento fabril 1918 (35), 41–3.

A series of analyses made by **G. Chavanne, L. P. Clerc** and **L. J. Simon**[1] on German aviation gasoline show these fuels to have a marked regularity of composition. The samples averaged a content of benzol 2.62 per cent, toluol 4.25 per cent, xylols 1.6 per cent. Alicyclic constituents amounted to 40 per cent and acyclic hydrocarbons, 50.5 per cent, as found by difference.

G. E. Heyl[2] states that the yield of lighter liquid hydrocarbons in fractionally distilling heavier hydrocarbons (mineral oils, coal oils, coal-tar oils, shale oils, and the like) is increased by impregnating the oil, before distillation, with a hydrocarbon gas or with hydrogen, without external heating. By preventing an increase in temperature during absorption, or, by reducing the temperature of the hydrocarbon, during absorption, below the prevailing temperature, the yield is said to be still further increased.

G. E. Heyl and **T. T. Baker**[3] manufacture motor spirit by dissolving hydrogen in liquid fuels such as gasoline, benzine, or alcohol. The liquid is sprayed into the gas within a chamber supplied with a safety valve. The solution may be passed over cold or heated aluminium or nickel in a tube to aid the retention of the gas. In a smaller apparatus twin opposing nozzles are used.

G. E. Heyl and **T. T. Baker**[4] propose the following mixture: 75–50 per cent gasoline, mixed with 25–50 per cent of the liquid obtained when the 170–230°C. distillate (middle oil) of coal tar is freed from naphthalene and tar acids. The mixture is filtered before use.

The ease with which carbon bisulphide is ignited has led to proposals for its use with other fuels of a less volatile nature. For example **A. A. Backhaus**[5] proposes a blended fuel suitable for use as motor fuel, formed of ethyl alcohol 25, gasoline 25 and carbon bisulphide 8 parts.

A fuel containing ether is suggested by **A. de-feo. Lopez.**[6] He partially converts alcohol into ether by bubbling the former through a mixture of alcohol and sulphuric acid at 100° to 150° C. (212° to 302°F.). The product is rectified and is mixed with from 10 to 40 per cent of alcohol and from 5 to 50 per cent of a suitable hydrocarbon distillate, the final mixture having a specific gravity of 0.730 to 0.780.

The Motor Truck[7] reports that some very interesting trials have been conducted by **Dieterich** with benzol and other fuels on an Opel car with an engine having cylinders 70 millimeter bore by 100 millimeter stroke with standard type of carburetor. The tests were made on a stretch of road 10 kilometers in length under equal conditions regarding

[1] Compt. rend. (1919), 169, 693–5; Chem. Abs., 1920, 464.
[2] J. S. C. I., 1918, 49 A; British Patent 111,933, Jan. 5, 1917.
[3] British Patent 11,756, May 20, 1913; Chem. Abs., 1914, 3628, 1914, 2241.
[4] Chem. Abs. 1916, 1266; British Patent 21,738, Oct. 29, 1914.
[5] Chem. Abs. 1920, 463; U. S. Patent 1,324,765, Dec. 9, 1919.
[6] J. S. C. I. 1919, 891 A; British Patent 133,434, 1918.
[7] Nov., 1913, p. 876.

temperature and weather. The results obtained with the different mixtures are as follows:

1. Ether. — Ordinary ethyl ether made from alcohol and sulphuric acid, containing about 64.9 per cent of carbon, 13.5 per cent of hydrogen and 21.6 per cent of oxygen; specific gravity, 0.718 to 0.725; calories, 9000 per kilogram. Used as fuel, unmixed, quickly stalled motor, mainly by reason of the great cooling produced by the rapid evaporation of this highly volatile liquid.

2. Petroleum Ether. — Propane, butane, pentane (mainly the latter), containing 85 per cent carbon, 15 per cent of hydrogen; specific gravity, 0.650 to 0.680; calories, 11,000. Results poor, as under 1.

3. Light Gasoline. — (Hexane, heptane and octane), carbon, 85 per cent; hydrogen 15 per cent; specific gravity, 0.680 to 0.720; calories, 9500 to 11,000. Produced a ma imum speed of 50 kilometers per hour with a consumption of one liter for eight kilometers. The usual advantages over benzol and heavy gasoline in the way of responsive acceleration and the greater power arising from rapid flame propagation.

4. Heavy Gasoline. — (Octane and higher grade paraffin), carbon, 85 per cent; hydrogen, 15 per cent; specific gravity, 0.730 to 0.760; calories, 10,500. Produced a maximum speed of 44 kilometers and a consumption of one liter for seven kilometers. Motor sluggish and acceleration slow.

5. Benzol. — (Benzene); carbon, 92 per cent; hydrogen, eight per cent; specific gravity, 0.8997; calories, 9500 to 10,000. Gave nine kilometers to the liter but a maximum speed of only $42\frac{1}{2}$ kilometers. Same drawbacks as with heavy gasoline.

6. Heavy Gasoline and Ethyl Ether. — Equal weight parts. Results poor; very little power.

7. Same Ingredients. — Proportion 1:1.5. Results poor, showing ether to be useless for admixture, apart from price consideration.

8. Heavy Gasoline and Petroleum-ether. — Equal parts; specific gravity, 0.701; calories, 10,000. Gave eight kilometers to the liter, maximum speed 45 kilometers. The acceleration was better than with heavy gasoline alone.

9. Same Ingredients. — Proportion 1:15. The results were almost as poor as with petroleum-ether alone.

10. Benzol and Petroleum Ether. — 1:1.5; specific gravity, 0.705; calories, 10,750. Gave eight kilometers to the liter; maximum speed 48 kilometers. Acceleration and results generally better than with benzol alone.

11. Same Ingredients. — Equal parts; specific gravity, 0.725; calories, 10,500. Gave eight kilometers to the liter; maximum speed

50 kilometers. Took grades on third speed which with ordinary gasoline required second speed. An important improvement upon unmixed benzol.

12. Same Ingredients. — Proportion 2:1; specific gravity, 0.797; calories, 10,300. Gave a little more than eight kilometers per liter and a maximum speed of 54 kilometers. Took all grades with higher gears than possible with other fuels. Good acceleration and lively explosions. Better than ordinary gasoline of 0.680 to 0.720 gravity.

The supplies of benzol vary very considerably in quality, and in view of the position that benzol seems likely to take as a motor fuel, some standard of composition should be decided upon. The best volatility and the permissible amount of impurities such as sulphur should be ascertained and fixed; there should also be some limit to the amount of toluol which it is necessary to add to keep the fluid liquid at low temperatures. The worst feature in connection with benzol is said to be its smell, but it is a fuel which must be encouraged by all possible means.

The Use of Naphthalene.[1] — Some attention has been given to the use of naphthalene as a fuel. A trial was carried out in Paris with a two-cylinder Renault cab fitted with a special carburetor consisting of a melting receptacle in which the supply of melted naphthalene is maintained by the exhaust at a heat above its melting point, and from which it is conveyed to a heated float feed carburetor. The engine has in the first instance to be started on gasoline in order to heat up the naphthalene. The time occupied in running on gasoline before the naphthalene can be switched on is 13 minutes 37 seconds. A stop of 10 minutes can be made without any further use of gasoline, while a stop of 16 minutes necessitates its use. The consumption worked out at 14,228 kilograms for 100 kilometers, at an average speed of 34.4 kilometers per hour. The price of the fuel was six francs per 100 kilograms, bringing the cost per 100 kilometers up to 0.85 francs, to which must be added the gasoline for starting.

In another test conducted by the Automobile Club of France, a car when running on naphthalene[2] showed an economy of 60 per cent over gasoline. In Germany the Gas Motoren Fabrik Deutz con-

[1] Motor Truck, *ibid.*

[2] Naphthalene was placed on the market in France a few years ago (Chem. Abs., 1913, 3223; Anon. Petroleum Rev. 28, 672) as a suitable substitute for motor spirit. It has a comparatively high volatility and a sufficient degree of calorific power. The annual output of naphthalene in France was given at that time as 14,000 tons. Some defects of it, namely, its high melting point are now being obviated by using it with benzine, benzol, petroleum, etc., and such mixtures are said to work very well in carburetors.

structs a stationary motor specially designed for this fuel. The production of naphthalene in Great Britain is about 126,000 tons, in Germany 175,000 tons, and in France 30,000 tons. The melting temperature is 49.2° C. melting point of pure substance is 80° C. and boiling point 218° C. The combustion of naphthalene is very similar to that of benzol and with practically the same heat value. The price of naphthalene in Great Britain has been as low as 75s per ton, and its production is stated to be considerably greater than that of benzol, but to convert it into practical fuel for motors is more the work of the chemist than the engineer.

The residue obtained from a crude benzol still of a Simon-Carvé's plant, known as naphthalene oil, is cooled and drained off from naphthalene and, according to **F. Spicer** and **H. Jackson** [1] the oil is distilled till the whole of the lighter oil and heavy naphtha and a small portion of naphthalene are driven off, and this distillate is washed and treated with acid, soda, and water, distilled again up to 190° C. and mixed with about one-twelfth part by weight of crude benzol or gasoline for use as a gasoline substitute.

"Energizing" Gasoline.[2] A good deal has been heard about energizing, or "doping" gasoline by, among other substances, picric acid which contains 48 per cent of oxygen, but does not readily dissolve in gasoline. Ammonium nitrate containing 60 per cent of oxygen is another suggested energizer, but this again is only slightly soluble in gasoline and the same difficulty has to be faced with acetylene gas. It is, of course, oxygen that is required, and the only known means of admitting this is stated to be through the inlet pipe.

In order to increase the proportion of oxygen in explosion mixtures, hydrocarbon vapor and moisture are subjected to electrolysis by **H. Csanyl**[3] while being led to the point of combustion, in order to decompose the water in the mixture and augment the proportion of oxygen in the mixture.

Both in France and Germany the conclusion has been arrived at that if alcohol is to be used it must be enriched or blended, and benzol has been tried for this purpose. The 'Bus Company in Paris has made extensive trials of mixtures of alcohol and benzol, in the proportions of 50 per cent, the consumption per kilometric ton being 0.09 liters. These motors were worked at a compression of about 400 pounds per square inch and ran at 900 revolutions per minute. They were fitted with an automatic regulator to prevent any increase. The most efficient

[1] J. S. C. I. Vol. 38, 1919, 621 A; British Patent 129,010, Sept. 19, 1917.
[2] *Ibid.*
[3] Chem. Abs. 1920, 1437; U. S. Patents 1,333,836 and 1,333,837, Mar. 16, 1920.

speed was found to be 650 revolutions per minute. Experiments have also been conducted with a mixture of acetylene gas and alcohol. In the **Barker** and **White** system diluted alcohol is sprayed on to calcium carbide. It would appear that the addition of acetylene adds con-
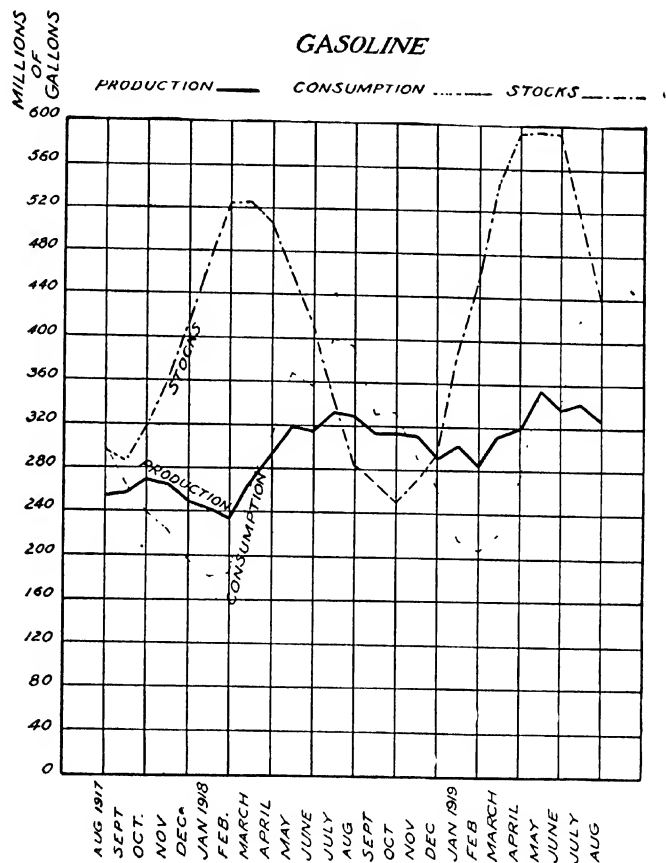
Fig. 4. — Chart showing relative magnitudes of gasoline consumption, production and stocks on hand in United States over a period of two years (1917-18-19).

siderably to the speed of ignition of the vapor. Picric acid has also been suggested as an enricher of alcohol, and investigation in this direction has resulted in the conclusion that it is not practicable for the reason that picric acid when mixed with the water in the alcohol has a corroding effect on metals.

It appears that cyclic hydrocarbons are conducive to smooth running

Kettering [1] states that forty per cent of benzol mixed with ordinary kerosene makes an engine operate with entire satisfaction and that if the engine in which this fuel is used is operating at or near its full load, no bad results will be experienced in the way of carbon deposits, etc. When added to gasoline in considerable proportion, kerosene gives
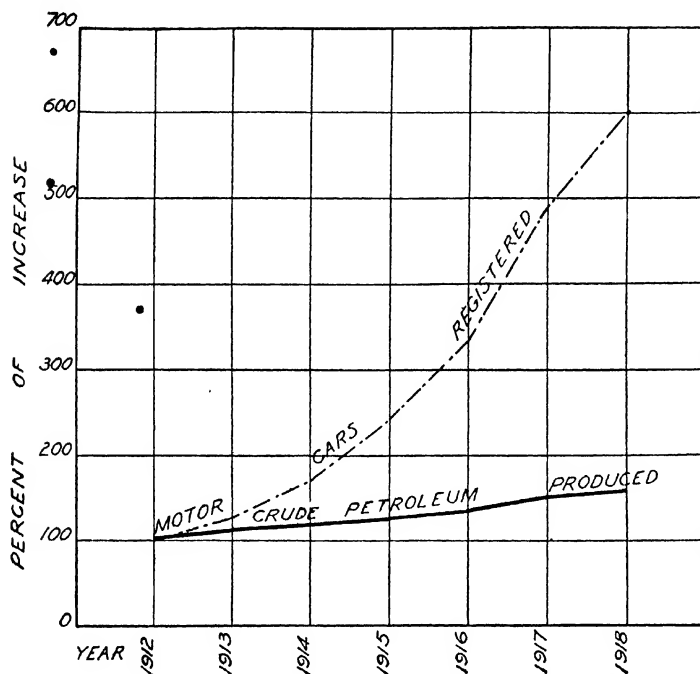
Fig. 5. — Graphic representation of increase in motor car registration as compared with increase in crude petroleum production.

trouble under high compression by producing an engine knock after ignition. This usually occurs at about one-fourth of the downward travel of the piston and is supposedly due to detonation following normal combustion or flame propagation. Benzol, iodine, ethyl iodide and in fact any substance which burns slowly so as to retard combustion will reduce the tendency of detonation and minimize the knock. Kettering [2] remarks that knocking in an internal-combustion engine has recently been shown to be due to the nature of the combustion, which probably

[1] J. Soc. Automotive Engineers, 1919, 199.
[2] Oil & Gas Journal, 18, No. 14, 62, 64 (1919); Chem. Abs. 1919, 2591.
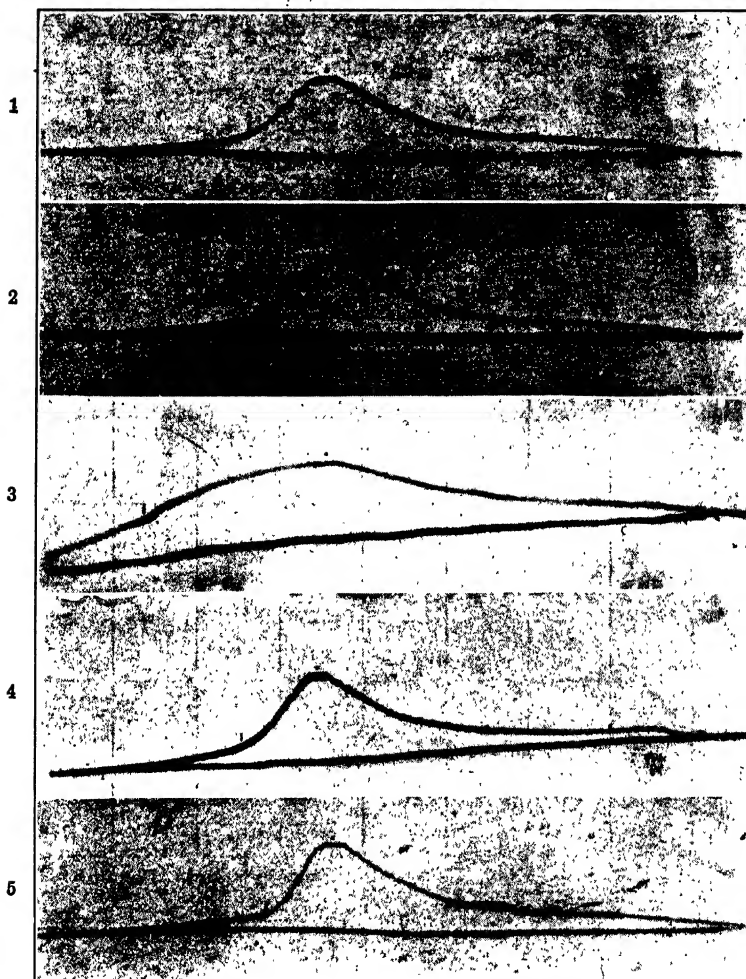
Fig. 6. — Indicator cards taken from Delco-light engine

In each case the vertical dash indicates the point of ignition and the dot the top dead center. The compressions are made on a uniform time basis and are not therefore directly comparable with the usual pressure volume reproductions

1 Alcohol — This card shows no very rapid rise in pressure, with consequent smooth operation.
2. Benzol — This fuel possesses pressure-producing characteristics similar to alcohol
3. Carbon Bisulphide — Note the very early "pre-ignition" *without* any consequent "knock" or rapid pressure rise, showing conclusively that "knock" is *not* caused by "pre-ignition," as has often been supposed
4. Commercial Gasoline — No evidence of "knock"
5. "High Test" Gasoline — Pressure rise is rapid, but there is no indication of "knock," further indicating that "knock-producing" quality is independent of either gravity or volatility of fuel.
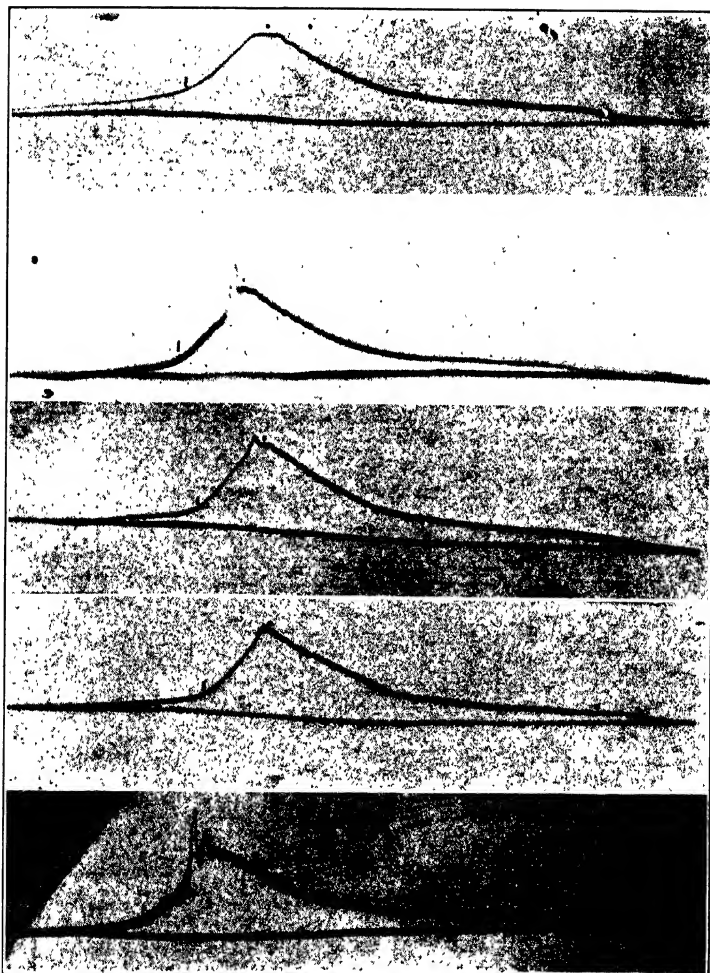
[1] Kettering, J. Soc. Automotive Engineers, 1919 (5) 198, 199. Cut fur-

using various fuels. 50-lb. compression pressure.[1]

sion line begins at left end of card and is followed successively by combustion and expansion lines The card diagram The following explanatory paragraphs for the different fuels are arranged in the same order as th of the cards

6. "Hecter" 70 per cent Cyclohexane and 30 per cent Benzol — Note the flat combustion line without an; very sudden rise in pressure This is conducive to a very smoothly operating engine

7. Kerosene — Note peak indicating sudden rise in pressure and causing "knock." The latter is *not* caused by "pre-ignition"

8. 3½ per cent Aniline and 96½ per cent Kerosene — Addition of aniline has nearly eliminated the pressure peal and consequent knock.

9. 5 per cent Ethyl Iodide and 95 per cent Kerosene — The peak and the consequent "knock" are substan tially eliminated by the use of ethyl iodide

10. 25 per cent Sulphuric Ether and 75 per cent Kerosene — Note that addition of a considerable percetang of a highly volatile liquid, sulphuric ether, has accentuated the peak and the consequent "knock," show ing that volatility of fuel is not a measure of its "knock-producing" characteristic.

nished through the courtesy of the Society of Automotive Engineers.

is influenced by the molecular structure of the fuel. If the compression is lowered in an effort to use low-grade oils, carbon will be deposited. However, certain substances can be added to such oils that will remove the knocking propensity. Thus 40 per cent of benzol added to kerosene makes a satisfactory fuel. Kettering observes that the oil refiners' problem is to learn what compositions will give best results, and at the same time carefully to study the products of combustion when different fuels are used.

The preceding indicator cards, show the behavior of various fuel mixtures and the suggested method of study [1] (Fig. 6).

T. Midgley, Jr.,[2] uses kerosene and states that " fuel knock " of internal combustion engines operating with kerosene under 70-75 pounds compression per square inch is avoided by the addition of about an equal quantity of benzol to the kerosene used. Small amounts of acetone or naphthalene may be added to minimize the deposition of carbon in the engine.

Wingett[3] proposes to mix kerosene with toluene and to slightly nitrate the mixture by treating with a small amount of a mixture of sulphuric and nitric acids, finally distilling the reaction product.

The U. S. Industrial Alcohol Company [4] proposes a fuel comprising gasoline, kerosene or other petroleum distillate, an alcohol such as ethyl or methyl alcohol and an aromatic nitro compound. Trinitrobenzol or trinitrotoluol are recommended and serve to blend the alcohol and petroleum distillate. Other blending agents, e.g. benzol, toluol, phenol, cresol and acetone may be used.

J. Andrews[5] obtains a power oil by heating naphthalene under reduced pressure, at 77-82°, with 0.4 per cent kerosene and the distillation product from sulphur and aqueous ammonia or a mixture of potassium nitrate and ammonia. The resulting volatile oil is purified with sulphur dioxide under pressure. It distills at 82-149° C. and has specific gravity 0.74.

C. F. Killar[6] sprays a liquid hydrocarbon oil in an atomized condition into a vessel filled with a gaseous hydrocarbon, e.g., acetylene. To prevent subsequent separation, a small quantity of ether, acetone or alcohol is previously added to the liquid hydrocarbon.

C. White and **C. F. Killar**[7] make an inflammable substance for use

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[1] Kettering. *ibid.* pp. 198, 199.
[2] Chem. Abs., 1919, 1636; U. S. Patent 1,296,832, Mar. 11, 1919.
[3] U. S. Patent 1,185,747, June 6, 1916.
[4] Chem. Abs. 1920, 2256; British Patents 140,796 and 140,797, March 25, 1920.
[5] Chem. Abs., 1915, 1389; French Patent 466,050, Dec. 11, 1913.
[6] J. S. C. I., 1917, 957; English Patent 107,217, May 19, 1916.
[7] J. S. C. I., 1917, 540, British Patent 105,256, Apr. 1, 1916

as fuel for internal combustion engines by dissolving a gaseous hydrocarbon (preferably acetylene) and gasoline in a mineral oil hydrocarbon fraction, the latter being preferably a petroleum fraction having specific gravity 0.775 to 0.780, boiling point about 150°–230° C. (302°–446° F.), and flash point 79° F. (26° C.). Liquids such as ether, alcohol or acetone may be added to retain the gaseous hydrocarbon in solution.

Winch [1] produces a liquid fuel for use in internal-combustion engines by heating bituminous coal in a retort sufficiently to drive off smoke-producing constituents as gases or vapors and then absorbing the latter in hydrocarbon oils, for example, petroleum, naphtha or xylene.

Mueller [2] makes motor fuel consisting of a mixture of anthracene oils dissolved in the light oils derived from the fractional distillation of coal tar with the products of the distillation of crude petroleum up to 350° C. (662° F.).

Fayd'herbe [3] makes fuel consisting of ethyl ether, 10–60 per cent, a petroleum fraction of relatively high flash point, for example, kerosene, 5–30 per cent, and alcohol of not less than 36° Cartier (specific gravity, 0.84), 30–80 per cent.

Whitaker [4] states that alcohol is used in conjunction with kerosene, benzol and heavier hydrocarbons to make motor fuel.

The fact that ordinary gasoline and alcohol are not mutually soluble, that is they do not " mix " has rendered it necessary to employ a third substance which will render the alcohol and gasoline or kerosene compatible with each other. A relatively large proportion of benzol will answer the purpose. Some substances, however, will accomplish the result when used in a relatively very small proportions. Castor oil and camphor have been used for this purpose.

A. A. Backhaus [5] suggests a liquid fuel mixture, adapted for use in burners or motors made from gasoline 25, kerosene 25, ethyl alcohol 25 and linolic acid, linolenic acid and oleic acid 12–13 parts. The acids may be obtained from linseed or rape oil.

In another proposal, castor oil is the substance used to make the gasoline and kerosene compatible with alcohol.[6] The proportions are:

Gasoline or kerosene ⎱
Ethyl alcohol ⎰ equal quantities.

Castor oil $\frac{1}{2}$ per cent.

[1] Chem. Abs., 1919, 2125; U. S. Patent 1,304,433, May 20, 1919.

[2] J. S. C. I., 1919, 404 A; U. S. Patent 1,297,388, March 18, 1919.

[3] J. S. C. I., 1919, 245 A; British Patent 123,450, April 22, 1918.

[4] Hearings before the Committee on the Judiciary on Enforcement of Prohibition, Serial 1, Part 2, June 12 and 14, 1919.

[5] U. S. Patent 1,306,244, June 10, 1909; Chem. Abs., 1919, 2125.

[6] Backhaus U. S. Patent 1,296,902 March 11, 1919.

P. Suchy [1] proposes dissolving in fuel hydrocarbons gallic acid $(HO)_3C_6H_2COOH$ or other substances containing the group OH, in combination with carboxylic acids or esters and distilling with a reflux condenser. In an example, illuminating oil, light benzine, ethyl acetate, ether and gallic acid are distilled together.

B. O. Jenkins [2] mixes a distillate from coal tar or coke oven tar, for example, benzol or naphtha (25, 33, or 50 per cent) with a volatile alcohol (for example, 74, 66, or 49 per cent of ordinary alcohol) and about 1 per cent of camphor, and the mixture is distilled to obtain a fuel of high flash point.

A. A. Backhaus [3] proposes a mixture, for use as a fuel in burners or motors, formed of ethyl alcohol 25, kerosene 25, gasoline 25 and chloroform, carbon tetrachloride, tetrachlorethane $C_2H_2Cl_4$ or trichlorethane $C_2H_3Cl_3$ 9 parts. Either gasoline or kerosene may be used instead of a mixture of both in forming the fuel.

R. Wood [4] mixes about equal parts of alcohol and ether, together with small proportions of ammonia, NH_3, and oxide of arsenic, As_2O_3, to prevent corrosion of the engine and to render the product non-potable.

E. Humboldt [5] has made a series of experiments with the object of testing the efficiency of various mixtures of kerosene, gasoline, or benzol, with alcohol and ether in the automobile and motorcycle engine. A mixture consisting of alcohol 1, ether 2, and " engine distillate " (kerosene) 24 parts, or in place of the kerosene 25 to 40 parts of gasoline, caused the engine to start more easily than gasoline alone and to carry its load without trouble, and not only prevented a deposit of carbon but cleaned off previous carbon deposits. A relatively small amount of ether generates a sufficient amount of low boiling point products to insure a large explosive mixture and easy running at low temperatures. Mixtures containing 1 part of ether, 2 parts of alcohol and 24 parts of benzol are claimed to work best for these circumstances. If in this mixture, 1 part of alcohol and 2 parts of ether are used, the engine starts readily, but as soon as it begins to work the rapid evaporation cools the carburetor so that frost is deposited. Humboldt says that a jacket on the carburetor does not help unless there is a special provision for cutting down the amount of fuel. It is claimed that benzol dissolves the shellac coating on the carburetor float and that the latter should be made of metal or a single piece of cork small enough to allow for swelling.

[1] Chem. Abs., 1916, 1266; British Patent 22,191. Nov. 7, 1914.
[2] J. S. C. I., 1915, 216; British Patent, 3899, Feb. 14, 1914.
[3] Chem. Abs., 1919, 2590; U. S. Patent 1,313,158, Aug. 12, 1919.
[4] Chem. Abs., 1916, 1590; British Patent 24,262, Dec. 18, 1914.
[5] Chem. Abs. 1920, 1427; Power 1919 (50), 418-20.

Humboldt believes that the production of benzol appears certain to increase, that alcohol can be made at a profit for 25 cents per gallon, and ether for 30 to 35 cents by modern methods. With kerosene at 13 cents per gallon, alcohol at 45 cents, and ether at 60 cents, the cost of the mixture first mentioned above would, it is said, fall below 18 cents.

F. Gruetzner[1] maintains that the Diesel principle, though theoretically and mechanically possible, cannot be used in automobile motors on account of the complication caused by the compressor and the use of compressed air.

It is said that the solid-injection system developed in recent years is so simple in design and operation that its adoption for high speed use offers no serious difficulties. It requires a compression of at least 350 lb. per sq. in. and injection of the fuel oil near the dead center of the compression stroke. The ignition pressure rises to between 400 and 500 lb. sq. in. Careful straining of the fuel oil is essential. A strongly designed fuel pump is needed to take care of the high pressures and speeds; also a carefully manufactured spray valve. The ignition is caused by the heat of compression. No spark plugs are necessary and any crude oil can be burned which is fluid enough to run through the pipes. The system itself is developed. Gruetzner considers the time is ripe to adopt it for the automobile engine and thus secure the safety and economy of the large oil engine.

The shortage of gasoline in Great Britain during the war led to extensive investigations for substitutes, among which were ordinary illuminating gas and producer gas.[2] A report has just been published by the committee appointed to investigate the subject.[3] The committee considers that gas traction is as safe as the ordinary form even when unprotected and exposed flexible containers are used. In its newer forms it is well worth consideration as an alternative of electric, gasoline or steam traction. Common city gas is estimated to be equivalent to gasoline in the proportion of 250 cubic feet of the former to one gallon of the latter. Presumably, these being English data, the city gas is more largely hydrocarbons than much of the gas supplied to American cities, and the gallon may be the imperial gallon of ten avoirdupois pounds. It is recommended, however, that gas bags should be replaced by rigid or semi rigid containers, whenever a compression plant can be installed, but it is not considered advisable that any existing plant for gas traction should be abandoned at this time.

David J. Smith,[4] who made many of the experiments in the matter, states that it is possible to run satisfactorily in competition with gasoline motor vehicles by producing gas made on the vehicle, using anthracite, coke or charcoal. He states that the cost of running a truck with

[1] J. Soc. Automotive Engineers 1919, 207.   [3] *English Mechanic,* 1919 (110), 31.
[2] J. Frank Inst, 1919 (188), 566.   [4] *English Mechanic,* 1919 (110), 45.

anthracite at 50s. ($11) per ton was equivalent to gasoline at 5.4d. (11 cents) per gallon, the commercial rate of the gasoline being taken at 2s. 6d. (about 60 cents) per gallon. He claims that a producer can be made according to his designs that will occupy no loading room on the truck, and free access to the equipment is secured. In case of trucks the weight of the equipment for producing the gas does not exceed 2 per cent of the weight of the loaded vehicle. The method is applicable to boats and tractors, the small size of the plant rendering it suitable for applications to which formerly producer gas apparatus could not be applied. **D. J. Smith**[1] sets forth the following advantages for producer gas: — Home-produced fuels, some of which are even at present waste products, can be used. There is no fire risk. Producer gas requires no labor for its production like coal gas. No gas bag is required. A vehicle can travel the same distance as on gasoline without taking in fresh fuel. The gas is of uniform quality, so that mixture troubles are eliminated. It is the cheapest source of power for motor vehicles known at present, and with coal at 40s. per ton is equal to gasoline at $2\frac{1}{2}d$ per gallon when used in the same engine. A gas producer is lighter and smaller than a compressed gas installation. It requires no pressure, and is therefore free from danger. Against the above the following disadvantages must be considered. It takes from 15 to 20 minutes to start from cold when using a producer. The extra weight of the plant has to be taken into account. Periodical cleaning is necessary. From 3 to 4 minutes is required to start after a lengthy stop. There is an increase of 75 per cent in weight of fuel, including water, to cover any given distance as compared with gasoline. The following comparisons are given for a five-ton commercial truck.

	Steam	Gasoline	Producer gas
Price of fuel	50s. per ton	3s. per gal.	55s. per ton
Cost in pence per gross ton mile .	0.31	0.66	0.048
Cost in pence per net ton mile	0.75	1.20	0.091

Smith's producer has been designed to do away with a thick fuel bed and to burn any volatile matter so completely that a bulky water scrubber for the gas will not be needed. The fuel bed is only about 6 inches deep and practically continuous feeding of fuel and discharge

[1] J. S. C. I. Vol. 39, 1920, 146 A; Inst. Automobile Eng. Jan. 8, 1920; Engineering, 1920, 109, 59–64, 92–95.

of ash are maintained by coupled feed and discharge valves. The fuel ignites at once, and the ash is not allowed to rest long enough to fuse into clinker. The only impurity in the gas is a little of the fine dust of the fuel carried over by the draught, and the gas is purified by passing it through a dry tubular scrubber heater where the water for the producer is pre-heated. The scrubber is easily cleaned out and the producer itself is jacketed, air being passed through the jacket to the water saturator and then to the producer. The whole apparatus weighs 200 to 300 pounds, and is compact enough to be carried on the dashboard of the car. The fuel (anthracite, coke, charcoal, or prepared peat) is carried in a bunker under the hood over the driver's seat, and is fed by gravity; the water is carried under the seat. Both vehicle and engine ought to be specially designed for use with producer gas, but very fair results have been obtained with a gasoline engine; the cost per gross ton mile in the same vehicle and engine was found to be 1.45d with gasoline against 0.0856s with producer gas. The producer gas is better adapted to the larger and heavier commercial class of vehicles, and if generally adopted would increase the amount of gasoline, benzol, etc., available for the lighter pleasure cars. Experiments have shown that no danger is to be apprehended from excessive escape of carbon monoxide, even when the vehicle is standing. Anthracite in the form of "beans" which pass a $\frac{3}{4}$- or $\frac{7}{8}$-in. screen is the most satisfactory fuel, but coke may be used, although it contains a good deal more ash and sulphur and does not feed so easily. Charcoal is a good fuel but is bulky. Peat briquettes which have had the objectionable volatile matter driven off by heat are very satisfactory. The best results are obtained with a fuel bed of 6 inches for anthracite, 7 for coke, 4 for charcoal, and 2 or 3 inches for prepared peat.

W. R. Ormandy[1] states that illuminating gas has been used quite successfully as motor fuel, 250 cubic feet being equivalent to about a gallon of gasoline. Extension of this practice is dependent upon the discovery of suitable methods for carrying this fuel on the vehicle.

Under post-war conditions, England should produce 50,000,000 gallons of volatile coal-tar distillates, one-half to two-thirds coming from the 9000 coke ovens now in operation. Shales and cannel coal offer a possible source of motor fuel from English resources, which should be considered carefully. Alcohol is the only other source likely to be developed. Five per cent of the American grain crop it is stated would yield sufficient motor fuel to replace the gasoline now demanded in America. In certain English colonies in South Africa, corn can be grown successfully, in practically unlimited quantities at a price not exceeding £1 per ton. This is a cost of 3.25d. per gallon of alcohol for the raw material only. *One part of benzol and two parts of alcohol yield a fuel for existing motors with practically no*

[1] Chem. Abs., 1919, 1917; J. Inst. Petroleum Technologists 1918 (5), 33-69.

alterations in their construction. On the basis of the benzol available, the English demand could be practically met by this mixture The production of ether $(C_2H_5)_2O$, from alcohol to replace the benzene is a possibility.

The use of acetylene as a component of motor fuel is receiving considerable thought at the present time. One of the objects in view is the utilization of the detonating ability of acetylene in contributing rapid flame propagation to the combustion of the less volatile fuels. The difficulty seems to be the production of a sufficiently stable solution of acetylene, in alcohol for example, or alcohol-containing fuels.

U. Alvisi [1] seeks to avoid the inconvenience of a rapid consumption in the combustion of acetylene by acting on it with carbon dioxide in the moment immediately preceding ignition in the air. The action is said to take place in two stages, ethylene being the intermediate product, while methane and carbon monoxide are the end products. By varying the quantity of carbon dioxide it is possible, it is said, to obtain flames that are more or less hot, and therefore, more or less luminous. Experiments, it is claimed, demonstrated the practical application of the process and the economy resulting from the great duration of the flame.[2]

H. Grossmann [3] comments on the utilization of acetylene in Switzerland. The chief difficulties of using acetylene fuel in internal combustion engines are said to be that the compressed acetylene air mixtures are themselves violently explosive, and that the soot and possible acids produced by the combustion may corrode the motor. The first two difficulties can be overcome by diluting the acetylene with suitable gases or vapors; the soot deposition can be avoided by providing an ample supply of air. Air might be regarded as the simplest diluent to mitigate the violence of the explosion; it was found, however, that the combustion of air-acetylene mixtures was always too sudden. The acetylene can be generated on board, or it can be taken from steel cylinders containing compressed acetylene dissolved in acetone or in acetone substitutes. Such dissolved acetylene is relatively safer than gaseous acetylene. From the cylinder a 2-mm. steel or brass tube is taken to the reducing valve which is connected to the carburetor; no

[1] Chem. Abs., 1916, 1704; Rass. min. met. chim. 1916 (44), 1-3; Ann. chim. applicata, 5, 118-9.

[2] **Burrell and Oberfell** (U. S. Bureau of Mines Technical Paper 112 (1915). The Explosibility of Acetylene) report that the smallest proportion of acetylene capable of propagating flame in a mixture of acetylene and air is 2.53 per cent at atmospheric pressure, and that the low limit is not much affected by increased compression. The upper limit of explosibility is given as about 73 per cent.

[3] Chem. Abs., 1919, 1139; Schweiz. Bauzeitung, Oct. 5, 1918; Engineering (1918) (106), 469.

additional apparatus are required, and the car is always ready for starting and can go on until the cylinder is practically emptied. The disadvantages are that the cylinders are heavy and expensive and not generally obtainable. Journeys of thousands of kilometers were made with dissolved acetylene, the large cylinders giving a range of 120 km. As regards the generation of acetylene from calcium carbide on the car, although there are hundreds of generators none of those tested proved quite suitable as the acetylene has to be purified; the cylinder gas is said to be always pure. The army authorities stipulated that the use of acetylene should not involve any change in the mechanism and that the machinery should at once be ready for either fuel, acetylene or gasoline. Since the acetylene has to be diluted, one complication is unavoidable, whether acetylene gas or dissolved acetylene is to be used; for this purpose an additional tank is provided, and further a set of nozzles by means of which the diluent can be proportioned. A number of diluents appeared serviceable (alcohol, benzine, gasoline, light tar oils, naphthalene, water, etc.) and at least 20 or 25 per cent of these were required to make the combustion less explosive. In a Martini car of 12 to 16 hp. the change-over to the acetylene mixture was effected by substituting a nozzle of 0.50 mm. for the 0.85 mm. nozzle. The per cent varies with the nature of the diluent; but an experienced driver can soon adjust his motor to the new conditions. Most of the diluents could be used as such; naphthalene and water required preheating of the carburetor. Acetylene with 20 per cent of a mixture of equal parts of alcohol and light tar oil burned very well. Corrosion of the motor was not noted after two runs each of 1000 km. (motor fed with dissolved acetylene). The engine of a motor boat kept running for six to eight hours per day for one month on acetylene fuel was found in good condition, although the acetylene was generated in a common Tozzi apparatus and not especially purified. The engine did not run hot, except in one case when half of the radiator was covered by an iron plate. The consumption of lubricant remained normal. As regards fuel consumption, the tests indicate 1 kg. of acetylene is equivalent to about 2.5 kg. of benzine.

J. de Cosmo and H. Quinaux [1] manufacture a mixture of naphthalene and mineral oils which is stated to remain homogeneous and to possess the same viscosity as the mineral oil.

The Marchioness de Ahumada [2] adds to pure or denatured alcohol a mixture of gasoline, benzene or the like with ethyl ether or other ether and a small quantity of a solution of phosphorus in carbon bisulphide. A few drops of essence of pepper-

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[1] Chem. Abs., 1917, 1297; German Patent 292,223, March 18, 1914.

[2] Chem. Abs., 1916, 2401; British Patent 27,733. Dec. 2, 1913.

mint are added to the alcohol before mixing. The purpose of the phosphorus may be to prevent oxidation of the gasoline.

W. H. Stevens [1] makes a gasoline substitute as follows:

Crude petroleum . . . . .1 gallon
Gasoline........ . ...3 pints
Ether................... ....2 oz.
Pulverized alum. .... .2 drams.
Oil of citronella................................2 drams.

T. E. Rice [2] mixes kerosene 1 gallon, with methyl ether 4 ounces, and carbon bisulphide 8 ounces.

G. B. Selden [3] states that paraffin hydrocarbon liquids, though "inert" to other supporters of combustion such as oxygen, ozone or nitric oxide will absorb enough hydrogen peroxide to enable kerosene to burn cleanly in an engine, the theory being that 20 per cent oxygen in air is sufficient to burn the carbon in gasoline but not enough for the carbon in kerosene. About 0.5 per cent hydrogen peroxide is run in the air inlet of the engine; or the oil is mixed with it, allowed to stand and decanted. Benzoic and acetic peroxides are said to give similar results. The addition of peroxides and of naphthalene picrate to fuel oils is said to result in "an increase in power."

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[1] Chem. Abs. 1916, 692: U. S. Patent 1,165,462, Dec. 28, 1919.

[2] J. S. C. I., 1917, 921; U. S. Patent 1,230,924, June 26, 1917.

[3] Chem. Abs., 1914, 2244; Nat. Petroleum News, 5, No. 7, 39–42; Petroleum Rev., 29, 463–4.

CHAPTER II

THE TESTING OF MOTOR FUELS [1]

Mechanical Tests

The testing of motor fuels is a broad subject and may be viewed from several angles by as many different types of persons interested. The producer of gasoline and other motor fuels, the manufacturer of automobile engines and accessories, the chemist, the engineer and last but not least, the man who uses the fuel, — all of these consider the subject from their specific point of view.

The subject can be divided into at least two large divisions, first, those chemical and physical tests which show what classes of substances the fuel is composed of, and what substances or groups of substances compose those classes. For example, chemical tests endeavor to answer such questions as the following:

Is the fuel strictly a petroleum product? How volatile is it? How much of it will boil off between certain definite temperature intervals? Is it composed of light hydrocarbons found naturally in petroleum? Does it contain light hydrocarbons which have been made by decomposing or " cracking " heavy oils?

If the fuel is not derived wholly from petroleum, what is its derivation? Does it contain aromatic or coal tar oils, for example benzol; or does it contain substances which are not hydrocarbons? Does it contain for example, alcohol, or ether?

Motor fuels may be of such varied composition, and still be efficient, however, that chemical tests alone are not usually sufficient in order to determine their suitability. On the other hand, with a " simple " fuel, for example, a strictly petroleum product, a chemical examination ordinarily will tell, with certainty, whether the fuel is suitable for use in present types of motors.

The actual behavior of a fuel under operating conditions is, however, the ultimate test of its desirability and its relation to other fuels

[1] That portion of this chapter which relates to mechanical tests has been prepared in collaboration with Joseph Tracy, Automotive Engineer, 1790 Broadway, New York City, who maintains large mechanical testing laboratories at Rutherford, N. J.

in this respect. Properties such as ease of starting in cold weather, quick response to the throttle, or flexibility, smooth running at various speeds, power developed in relation to fuel consumed at various speeds and with different loads, tendency to deposit carbon, — these and other related considerations are best studied by an actual engine test. To be sure, these considerations are functions not of the fuel factor alone — engine construction being of the greatest importance — but even on the basis of fuel alone, engine tests are, at the least, equally as important as chemical and physico-chemical tests.

Engine tests to determine fuel characteristics and efficiency usually involve, as one of the principal determinations to be made, the power developed under various operating conditions, per unit volume or weight of fuel consumed, per unit time (e.g., per hour).

So far as the fuel side of the question is involved, engine tests are most significant when carried out on a comparative basis, that is when the fuel in question is tested in the same engine and under the same conditions in that engine, as a fuel possessing known characteristics. This follows, of course, from the fact that a fuel which gives excellent results in a particular engine may fall far below par when used in a different type of engine, or may, correspondingly, give better results.

Pounds of Fuel Consumed Per Brake Horsepower Per Hour. — To determine this quantity, use is made of a dynamometer, which is a machine for loading an engine and at the same time measuring the torque or turning effort produced by the engine under this load. By measuring the speed of revolution of the crank shaft at the same time, the energy developed by the combustion of fuel, communicated to the piston and finally appearing as useful work on the crank shaft, capable of transmission to the rear axle, is obtained.

It is a quantity which is intimately connected with the thermal value of the fuel and also with the   echanical and thermal efficiencies of the engine.

There are at least five different types of dynamometer, viz., the Prony brake, the hydraulic dynamometer, the fan dynamometer, the electrical dynamometer, and the " cradle " or torque reaction dynamometer. Description is limited to the electrical dynamometer.[1]

In testing large stationary engines the Prony brake was formerly used to a great extent but has been lately superseded by the hydraulic dynamometer. Regardless of the type of dynamometer however, the

[1] For a more detailed discussion of Dynamometers see
   Flather, " Dynamometers and the Measurement of Power,"
   Smith-Jervis, " Dynamometers,"
   Riedler A., " The Scientific Determination of the Merits of Automobiles."

principle of testing remains the same, i.e., the measurement of power developed.

The electric dynamometer consists essentially of a special electric generator, in which the field frame is so mounted as to be capable of rocking or oscillating freely in anti-friction bearings. The supports for these bearings are secured to a bedplate, and on an extension of this bedplate, or on another adjacent thereto, the engine to be tested is mounted on an adjustable stand, so that its crank shaft is in line with the shaft of the armature of the electric dynamometer. This armature is coupled to the engine shaft, and revolves inside the field frame of the

Fig. 7. — Sprague Electric Dynamometer.

dynamometer. The electrical inter-action between the internal revolving armature and the external field tends to turn the latter with a force exactly proportional to the torque transmitted to the armature by the engine.

By balancing the turning effort exerted on the external field, by means of a set of scales or weights, the turning effort of the armature can be measured exactly on such scales. The radial distance from the center of the armature shaft to the point of application of the scales which balance the rotative effort of the field is of course constant for any given type of machine. The horsepower developed by the engine then becomes

$$H.P. = 2\pi \times R \text{ (feet)} \times S \times W \text{ (pounds)}$$

When R = radius, or length of torque-arm
S = speed of shaft in revolutions per minute
W = weight shown on scales

The radial distance from the center of the armature shaft to the point of application on the scales is calle l the torque-arm, and is selected of such a length as to reduce the formula to the simplest terms.

The current generated in the armature is carried out of the dynamometer through flexible cables, so suspended as to present no retarding action on the motion of the field, and this current is absorbed in an adjustable resistor; and in certain cases it can be carried back into an electric circuit as useful power.

The load on the engine is regulated by varying the strength of the current, this depending upon the field strength of the generator and the electrical resistance of the resistor in which the energy is dissipated in the form of heat. By a combination of both methods of operation, very close regulation of the load and speed can be obtained. (See Fig. 7.)

The transmission of electrical energy from the dynamometer to the resistor does not enter into the calculation, and no corrections have to be made for the efficiency of the machine or its mechanical or friction losses.

In measuring the fuel consumption during a test, the fuel is contained in a covered vessel supported on a platform balance. To facilitate calculations, the beam of the balance should be divided into pounds and hundredths of a pound. The carburetor is connected with the fuel container by means of flexible tubing.

In making a run, using the type of dynamometer described there are three main observations to make:

(a) Weight of fuel consumed during test.

(b) Speed of shaft in r.p.m.

(c) Weight necessary to balance the torque exerted by the dynamometer shaft.

In comparing two or more fuels it may be desirable to adjust the flow of cooling water to and from the engine jacket so that the rate at which heat is conducted away in this manner may be observed. Thermometers are inserted for obtaining the temperature of the water supply and discharge. By weighing the cooling water and taking an average temperature difference between that of the supply and discharge, the actual amount of heat lost in this way can be accurately measured.

By making a run, for six minutes at a given speed and constant load, and multiplying the weight of fuel used by ten, the fuel consumption per brake horsepower per hour is easily calculated. With a given fuel in any particular engine, there are certain mechanical conditions of operation which determine the fuel economy independently of the inherent nature and composition of the fuel itself. These are:

(*a*) Brake load.

(*b*) Speed of crank shaft.

(*c*) Throttle opening.

$$\text{Since horsepower} = \frac{\text{torque} \times \text{speed}}{\text{constant}}$$

for any engine the torque may be constant for a given range of speed. It should be stated that in determining fuel economy, tests are made at various speeds and at different loads.

In Figure 7a [1] it will be noted that the fuel economy is the same at 1200 as at 1400 r.p.m., and also that whereas the torque drops off about 5 pounds in this interval, the horsepower increases about 1.7 units. That is, for a given adjustment of the throttle, increase of speed beyond a certain point decreases the torque because the suction stroke is so much faster at the higher speed that not so much air and fuel are drawn into the cylinder and the subsequent explosion has, therefore, less energy. However, since horsepower depends on two factors, torque and speed, although there may be a speed beyond which the torque diminishes, nevertheless, maximum horsepower may be developed at speeds higher than correspond to a maximum torque. That is, an engine may develop its maximum horsepower at speeds where the torque is below its maximum. (See Figure 7a.)

In connection with the effect of increasing speed on decreasing torque, the viscosity or fluidity of a motor fuel is important since this influences the ease with which the fuel is ejected from the carburetor nozzle.

The fact that fuels, especially volatile fuels, have a self-cooling effect in vaporizing is very important. Under some operating conditions this cooling may often lead to a deposit of frost on the manifold tube. Obviously this retards vaporization and may even result in a precipitation of the heavier portions of, for example, commercial gasoline.

As a rule, in making fuel tests, fuel consumption is determined under the following conditions and for the purposes named:

(*a*) Wide open throttle with full load at various speeds within the range of the motor.

(*b*) Partly open throttle (or with partial load) at various speeds.

(*c*) In the case of a stationary engine, full and partial loads at constant speed.

(*d*) Throttling Test. To determine ability of engine to run slowly with throttle almost closed and with no load. This is also known as " idling test."

[1] Compiled by **Joseph Tracy,** Automotive Engineer, 1790 Broadway, New York City.

(e) Acceleration Test. To determine the ability of the motor to accelerate with comparatively small load, from " idling " at low speed to the maximum speed.
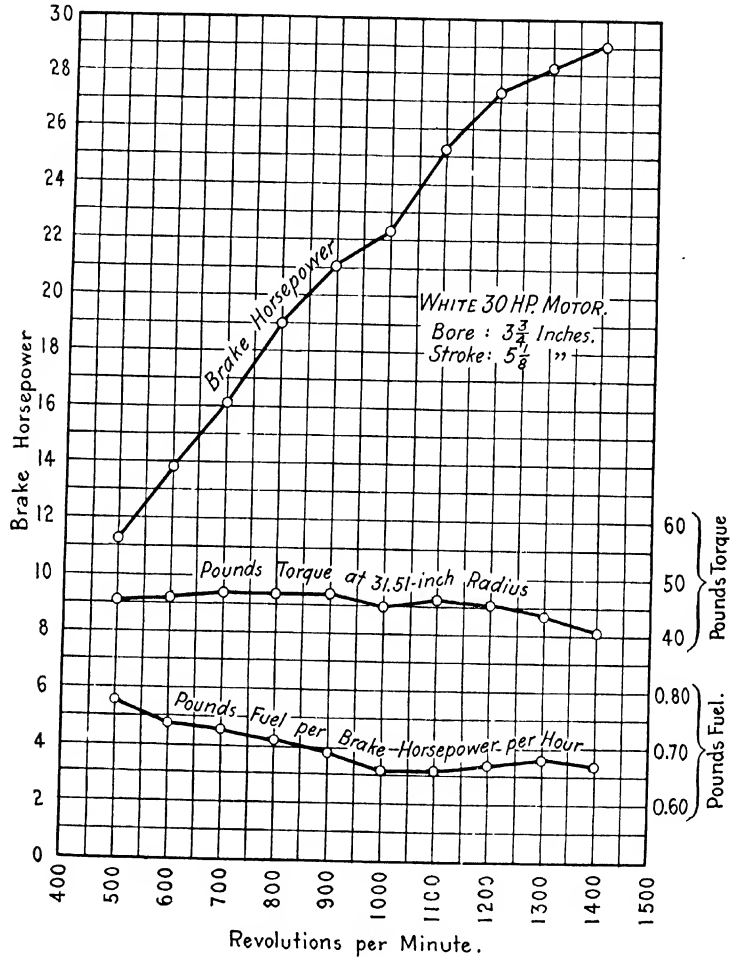
Fig. 7a. — Curve correlating speed with fuel economy, torque and horse power. Compiled by Joseph Tracy 1790 Broadway, New York.

The following observations are also important:

(a) Observation of amount of smoke in the exhaust during the various tests referred to.

(b) Extent or amount of carbon deposit on the pistons and interior

surfaces of the combustion chambers, under various condi-
tions of speed, load and throttle opening.

(c) Effect of the fuel on the surfaces of the cylinder walls, valve
faces, and valve seats.

(d) Effect of the fuel in diluting the lubricating oil in the crankcase,
in the event of leakage taking place past the pistons.

Strictly comparable fuel efficiency tests [1] on the basis of the con-
ditions just specified will usually place one in a position to state the
relative merits of the fuels tested.   It is the fuel which shows the best
efficiency under as many different operating conditions as possible that
should be selected as the fuel with the most desirable characteristics.

A fairly considerable amount of material has been written concern-
ing the use of the manograph for studying the explosions which occur in
internal-combustion engines.   The manograph is intended to serve, in
the case of internal-combustion engines, a purpose similar to that which
is exercised by the ordinary indicator with regard to steam engines.
Regardless of the type of manograph used the primary object is to
secure as faithful as possible a picture of the pressure-volume changes
which take place during the period of one complete cycle.   To this end
inventors and designers of manographs have endeavored to reduce to
the lowest possible minimum friction between the mechanism which
transmits and records the reciprocating motion of the piston as well as
the pressure variations.   It has been necessary, as well to design the
motion and pressure recording parts so that they have as little inertia or
lag as possible.   The spring which is used in the steam engine indicator for
assisting in recording pressure variation is entirely out of the question
for exercising a similar function in an internal combustion engine.   The
sudden development of pressure in the explosion engine necessitates a
device which will instantly respond to such rapid rises in pressure.
Some form of delicate diaphragm is usually employed for this purpose.

The motion of the diaphragm as well as the reciprocating motion
of the piston may be communicated to a mirror which is capable of
moving in two planes.   The mirror may be illuminated and a spot of
light is thereby reflected from the mirror to a ground glass plate similar
to the plate used in cameras.   Each motion of the mirror if recorded
independently of the other would produce a straight line on the ground
glass plate in the form of a moving spot of light, the line corresponding to
pressure changes being at right angles to the line recording the recip-
rocating action of the piston.   In practice, the motion of the mirror

[1] For an exhaustive series of tests of stationary gasoline and alcohol engines
see **Strong** (Bureau of Mines Bulletin 43 (1912) 132).

causes the spot of light reflected on the ground glass plate to trace
a diagram, which in the case of a complete cycle is a closed pressure-
volume diagram.

The form which the diagram takes is very instructive in recording
the nature of the explosions. The purpose of the manograph represents
an attempt actually to see or visualize what goes on inside the cylinder.
In connection with a study of the adaptation of any given fuel to a
particular type of motor it can readily be seen that the manograph is a
valuable instrument in the hands of one who knows how to use it and
to interpret its results. The use of the manograph, however, may be
considered to be an art requiring considerable experience on the part of
the operator.

Chemical and Physico-Chemical Tests

E. W. Dean [1] summarizes the desirable properties of gasoline as
follows:

1. The gasoline should not contain too large a percentage of highly
    volatile products, which tend to cause large evaporation losses
    and excessive danger in handling and storage, but should have
    enough volatile constituents to permit starting an engine under
    reasonably unfavorable conditions, without preheating.
2. The gasoline should not contain any considerable percentages
    of heavy or nonvolatile constituents, which after atomization
    into the engine cylinders can not be completely vaporized and
    burned.
3. The gasoline should not contain material that after combustion
    leaves a residue that collects in the motor.
4. The gasoline should be free from substances that attack metal,
    either before or after combustion. Unremoved acid (used in
    refining) falls under this head.
5. Neither the gasoline nor its products of combustion should
    have a strong or markedly disagreeable odor, as this is ob-
    jectionable to users of automobiles.
6. The gasoline should be free from noncombustible material such
    as water and sediment.

Discussing the testing and standardization of motor fuel **E. L.
Lomax** [2] states that the hydrocarbons likely to be found in motor
spirits are paraffins, iso-paraffins, naphthenes or cyclo-paraffins and
aromatic hydrocarbons. These show definitely that specific gravity

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[1] Bureau of Mines Technical Paper 214 (1919) p. 7.
[2] Pet. Rev. 1917 (37), 251–252, 269, Petroleum World 14, 477–482.

is no index of volatility. All specific gravities should be referred to 15.5° C. (59.09° F.). The Engler method of distillation clearly indicates the addition of low boiling products, but the liability to personal error is greater than in the Redwood method. The Redwood method should be run at the rate of 2.5 c.c. per minute and even a naked flame may be used but a gauze under the flask gives it protection. The final boiling point on gasoline should be raised to 170°–180° C. (338°–356° F.) 25–30 per cent over at 100° C. (212° F.). This would increase the percentage materially. Sulphur may be detected by the standard method of boiling with metallic sodium and testing with sodium nitroprusside. An approximate determination may be made by boiling with clean copper foil and comparing with results obtained on gasoline of known sulphur content. A more accurate determination calls for burning a mixture of gasoline and alcohol and absorbing the gases of combustion in N/16 sodium carbonate. The specially devised lamp is burned dry and then two small charges of alcohol are burned to clean gasoline out of the wick. After absorption the sodium carbonate solution is titrated with N/32 sulphuric acid.

The methods at present in vogue for the analysis of motor spirits are not fully satisfactory according to **H. Moore** [1] for the testing of mixed fuels such as will probably be extensively used in the future. The conditions existing in the engine and in the carburetor through which the fuels have to pass are the main factors in deciding the tests to which a motor spirit should be subjected. Specific gravity is stated to have little value as an indication of the quality of a motor spirit. The *viscosity* of all common fuels is very small, but this value may become important with future fuels. Heavy oils for Diesel engines may require suitable preheating to maintain the viscosity within reasonable limits. The *cold test* is important for fuel mixtures containing solid hydrocarbons in solution. For aero-engine fuels it is essential that the temperature at which solids separate shall be very low. The *coke test* consists in volatilizing the fuel in a platinum crucible and coking any residue remaining. Some of the heavier coal-tar distillates present in mixed fuels sold as "substitutes" yield appreciable quantities of coke. The *fractional distillation* test gives considerable information as to the ingredients present in a fuel mixture. *Latent heat of vaporization* is an indication of the cooling effect produced in the carburetor, and of the desirability or otherwise of hot air intake. *Iodine and bromine values* give information as to the method of preparation of petroleum spirits, but are not a direct indication of the behavior of a fuel in the engine. The *ultimate analysis* indicates the nature of the products present in the fuel, and

[1] J. S. C. I.; 1918, 681 A; Automobile Eng., Sept. 1918, 245–248.

allows of the calorific value and the weight of air required for combustion being calculated. The *temperature of spontaneous ignition* of a fuel ¹'determines the limits of compression pressure which may be employed. The most careful consideration is necessary in preparing mixed fuels to insure that the mixtures will stand normal compression pressures without pre-igniting. *Vapor pressure* determinations give direct information as to the probable behavior of fuels as regards easy starting and " flexibility." Benzol and good quality gasolines •have high vapor pressures, and the former also possesses the property of raising the ignition point of mixtures. It is therefore advantageous to mix benzol with heavy petroleum fuels (which, consisting mainly of aliphatic hydrocarbons, have low ignition points), and to employ light gasoline for " livening " heavy fuels of coal-tar origin, such as solvent naphtha, which consists mainly of aromatic hydrocarbons (largely xylol) and has a comparatively high ignition point. The *explosive range* must be considered in adjusting carburetting devices, so that the throttle scale may fall within that range, and the lower limit requires consideration in connection with vapor pressure for fuels, such as alcohol, which are only explosive in mixtures containing comparatively high percentages. *Velocity of flame propagation* is not easy to determine; it effects the correct angle of spark advance at any given speed. Fuels which possess slow speeds of flame propagation, and therefore require greater angles of spark advance can withstand slightly higher compression pressures than fuels of equal ignition point but possessing higher velocities of flame propagation. Calorific values (per weight) of motor spirits of any particular class do not vary greatly.

J. S. S. Brame [2] states that the rate of flame propagation in gasoline-air mixtures is an important consideration, determining as it does whether combustion has ceased before the end of the working stroke of the piston and how soon after ignition the maximum pressure is reached, which determines incidentally the point in the cycle where ignition should take place. Obviously, with an engine running at, say, 2000 r.p.m., a slow-burning mixture may even be alight when the inlet valve opens, with consequent firing back into the carburetor.

Moore [3] also states that spontaneous ignition temperatures [4] can be used as a means of deciding the maximum and minimum engine compressions suitable on gasoline and Diesel engines respectively when burning any given liquid fuel. By plotting the calculated values

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[1] H. Moore, J. S. C. I., 1917, 109–112.
[2] Fuel, London; E. Arnold, 1919, pp. 153–154.
[3] Engineer, 1917, 561; J. S. C. I., 1917, 861.
[4] See also J. S. C. I., 1917, 109.

of temperature and compression pressure, a curve is obtained which shows the theoretical maximum compression practicable in a gasoline engine, and which is also the minimum limit for the compression practicable in a Diesel engine, assuming that the temperatures represent the ignition point of the fuels. As several conditions cause interference with the working of this rule, the practical limits do not coincide with the curve. To obviate this difference practical curves applicable to engines operating on the constant volume and constant pressure cycles respectively, have been constructed from the results of engine trials on fuels of known ignition temperature. By the use of these curves the compression pressure of internal combustion engines can be directly ascertained by determining the ignition point of a fuel. Motor spirits of petroleum or shale origin do not vary in ignition point to any large extent. Benzol, alcohol, kerosene, and naphthalene possess widely varying ignition points which make adjustment of the engine compression advisable. Fuel oils derived from coal tar possess high ignition points, and mixtures are being marketed containing petroleum oils together with coal tar distillates. Such oils, if suitable as regards general chemical analysis, require examination as to ignition point; if the ignition temperature be high it will be necessary to make adjustment on Diesel engines, as otherwise in cold weather difficulty in starting will be experienced. By determining ignition points of mixtures of kerosene with tar oil and of Mexican fuel oil with tar oil, curves of ignition point against compression have been constructed. Mixtures containing half tar oil and half petroleum products have ignition points which are lower than the mean of the values for the two constituents. The admixture of a small quantity of either oil to the other causes the mixture to possess an ignition point differing from that of the main constituent.

To secure data for use in his experiments on the Diesel engine Moore [1] made a series of measurements of ignition temperatures of various oils. The apparatus consisted of a block of steel 4 inches in diameter and 3.25 inches deep so machined as exactly to receive a platinum crucible with a screw cover which served as the combustion chamber. Temperatures were measured by means of a thermocouple pyrometer fitted into the block as close as possible to the base of the crucible. A current of air or oxygen preheated to the temperature of the experiment was conducted into the crucible and when the temperature was constant a drop of the oil to be tested was introduced. By repeated experiments the minimum temperature at which ignition took place was rapidly determined. Following are results of a few measurements:

[1] J. S. C. I., 1917, 109; Chem. Abs., 1917, 1745.

Fuel	Temp. of ignition in Oxygen	Temp. of ignition in air
Crude petroleum (Texas)	.256° C. (493° F.)	387° C. (729° F.)
Crude petroleum (Borneo)	269° C. (516° F.)	380° C. (716° F.) -
Crude petroleum (Mexico).	.274° C. (525° F.)	424° C. (795° F.)
Ethyl alcohol	395° C. (743° F.)	518° C. (965° F.)
Turpentine	.275° C. (527° F.)	275° C. (527° F.)
Coke tar (Koppers)	195° C. (923° F.)	..
Blast furnace tar	498° C. (928° F.)	.
Benzene (100 %)	566° C. (1051° F.)	.. ...

It is concluded (1) that with increasing molecular complexity the ignition temperature rises; (2) that the ignition temperatures of aromatic compounds are much higher than those of aliphatic; and (3) that unsaturated substances ignite at lower temperatures than the saturated.

Newton and Williams [1] give the following items concerning physical tests of gasoline. *Distillation* is said to be the most important as it indicates clearly the quality of the gasoline. The *initial boiling point* is the temperature at which the first drop of condensate falls from the condenser. The *final boiling point* is the highest temperature reached in distilling a sample to dryness. Tagliabue's apparatus is used for gasoline distillation and five per cent temperature readings are made. The " *doctor test* " (i.e., test for sulphur compounds) is claimed by these writers to be next in importance to distillation. The gasoline is thoroughly shaken with a solution of sodium plumbite and a small quantity of flowers of sulphur is added. If neither the gasoline or sulphur is discolored the " *doctor test* " is satisfactory. The *color* is now generally taken with some type of colorimeter and not in a 4-oz. bottle. *Density, odor, per cent water*, and *foreign matter, chill test* and *calorific value* are also taken up, but are minor considerations. With casing-head gasoline the determination of *vapor pressure* is of importance because of shipping restrictions.[2]

[1] Chem. Abs. 1919, 659; Petroleum Age 6, No. 2, 11-4 (1919).

    [2] **A. Philip** urges (Inst. Petrol. Technol. Oct. 21, 1919; J. S. C. I. 1919, 939 A) the necessity for the adoption of standard methods for the testing and analysis of mineral oils. (1) Distillation tests on crude oil. — A specially designed topping still is described, which is heated on an air bath in which is situated a coil through which air is passed by means of an electric blower. The air stream is controlled by a gas current meter, and thus any predetermined volume of air may be circulated in a closed system. Losses are in this way greatly reduced and any water in the oil is quietly removed without risk of foaming or bumping. The gas current meter is a U-tube filled with lead shot. The resistance thus afforded controls the passage of air and once the appliance is calibrated a definite current can always be reproduced. The distillation, after " topping " for water, gasoline and kerosene, is continued in a steam still, which is provided with two internal baffles to prevent priming

The evaporation velocity of motor fuels has been determined by **K. Dieterich.**[1] Light, medium and heavy naphthas, benzol and alcohol have been investigated. A short, steep, straight curve indicates the best quality of fuel, while a long, irregular curve is characteristic of a fuel containing a high proportion of less volatile components.

McAffee[2] reporting on the quality of gasoline made by the aluminum chloride method, mentions the following methods of testing:

Color, odor, bromine number, " *Doctor test,*" *(acid) heat test, gravity* and *distillation test.*

Concerning the (acid) heat test and bromine value **Dean** and **Hill**[3] comment as follows:

Determination of Unsaturated Hydrocarbons

The (Acid) Heat Test. - A method largely used in the laboratories of refineries for determining the degree of unsaturation is the "acid heat test," which is practically identical with the Maumené[4] test,

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and an annular channel to prevent condensed liquid dripping from the roof into the heated oil.

(2) Vapor tension of motor spirit – An apparatus is described for the determination of the temperature at which the vapor tension of a spirit is equal to atmospheric pressure. This figure is stated to be the nearest approach to the "boiling point" of the gasoline

(3) Calorific value of motor spirit – The bomb calorimeter is used. About 0 5 gram is weighed out in a stoppered tube, which, together with 0.25 gram of naphthalene, is placed in the platinum crucible. On firing, the heat liberated by the combustion of the naphthalene vaporizes the gasoline and expels the stopper of the tube. Ignition of the spirit then takes place, with no possibility of loss, which is otherwise liable to happen in the interval between weighing the gasoline and closing the bomb.

(4) Free acid in oil fuels – Free acidity to alcohol and to water are determined and reported in terms of oleic acid.

Effect of moisture on flash points — A careful investigation has been made to determine the effect of moisture on flash points In general it may be said that for low-flashing distillates, e g , kerosene, the presence of water is scarcely likely to affect the result, seeing that, in the first place, water readily settles out from the oil, and, in the second place, the low temperature at which the oil flashes is insufficient to liberate an appreciable amount of water vapor. In the case of fuel oils, however, there may be emulsified water present, and at temperatures upwards of 150° F , this water has a decided effect.

[1] Petroleum, 1917, 12, 676; J. S. C. I., 1919, 244 A.

[2] Trans. Amer. Inst. Chem. Engineers, 1915 (8), 179.

[3] Bureau of Mines Technical Paper 181 (1917).

[4] Maumené, M., De l'analyse des huiles au moyen de l'acide sulfurique: Compt rend., t. 35, 1852, pp. 572–573. Leach, A. E , Food inspection and analysis, New York, 1914, 3d edition, p. 494.

sometimes used in the testing of turpentine and fatty oils. This method really involves measuring the heat of reaction of oil and acid, conditions being regulated so that the heat of reaction is proportional to the rise in temperatures.

The method is commonly applied as follows: 50 c.c. of gasoline is placed in a glass-stoppered bottle, 10 c.c. of ordinary concentrated sulphuric acid added, and the mixture shaken. The temperature is taken before the acid is added and then at intervals while the mixture is being shaken. As soon as a maximum temperature is reached the reaction is considered complete and the rise in temperature, generally expressed in Fahrenheit degrees, is called the " acid heat test " of the gasolene. " Straight " refinery gasoline generally has an acid heat test of less than 10° F. and the cracked products commonly marketed usually have tests not exceeding 30° or 40° F.

The difficulty with the method is said to be that gasoline is such a volatile substance that part of the heat developed is dissipated in causing vaporization, instead of producing a rise in temperature. The error thus introduced is not considerable when the acid heat test is low, but with even moderately highly unsaturated gasoline is so large as to make the results entirely unreliable.

Conclusions with regard to the merits of the acid heat test are briefly as follows: The test is of value only for gasolines of moderately low degree of unsaturation, and when operating conditions are so maintained that the rise in temperature is proportional to the heat of reaction. The container employed should always be of a standard heat capacity and fixed quantities of acid and gasoline should be used. The strength of the acid should be always the same and the rate at which it is added to the gasoline probably should be fixed. The rate of adding acid is a particularly important source of possible variation, because the course of the reaction is probably affected by the relative concentrations of unsaturated hydrocarbons and acid. The quantity of acid used should be sufficient to react with all the unsaturated hydrocarbons, but should not be unnecessarily large, as the excess acid absorbs heat and thus cuts down the temperature rise. The use of a vacuum bottle of about one pint capacity is decidedly advantageous in that heat losses through radiation are eliminated and its heat capacity, being small, is not liable to cause important variations. Simple shaking with a rotary motion is better than the use of a mechanical stirrer.

The experiments indicate that the acid heat test is less satisfactory in operation than the method of absorption by sulphuric acid and that the results are less reliable.

Bromine Absorption Method. — The method of **McIlhiney** [1] was selected as representative. This method involves absorption of bromine in a medium of carbon tetrachloride during a reaction period of thirty minutes. The excess of bromine is determined by adding potassium iodide solution and titrating the liberated iodine with standardized sodium thiosulphate solution. The proportion of bromine that goes to form substitution products instead of being directly added to the hydrocarbon molecules should also be determined. This is accomplished by a supplementary titration, with thiosulphate, of the iodine liberated when a neutral solution of potassium iodate is added to the reaction mixture. The true bromine addition value is found by subtracting twice the amount found by the last titration from the total quantity of bromine absorbed. The reactions involved are as follows:

1. Bromine addition (typical) —

$$C_2H_4 \quad + \quad Br_2 \quad = C_2H_4Br_2$$

Ethylene   Bromine   Ethylene
bromide
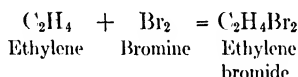
2. Bromine substitution (typical) —

$$C_2H_6 \quad + \quad Br_2 \quad = \quad C_2H_5Br \quad + \quad HBr$$

Ethane   Bromine   Ethyl bromide   Hydrobromic acid
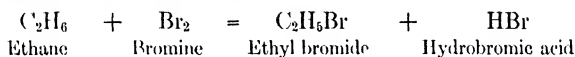
3. Determination of bromine substitution, which is equivalent to hydrobromic acid formation; the bromine addition value is the total bromine loss minus the sum of the equal quantities of bromine substituted and converted into hydrobromic acid —

$$6HBr + \quad KIO_3 + \quad 5KI \quad = 3I_2 \quad + \quad 6KBr \quad + 3H_2O$$

Hydro-   Potassium   Potassium   Iodine   Potassium   Water
bromic   iodate   iodide   bromide
acid
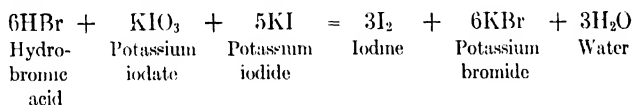
Comparison with Iodine Method. — Bromine numbers were determined by this method for a series of samples of varying degrees of unsaturation. With these samples the amount of bromine substituted proved to be practically a negligible quantity. Results of the tests are shown in the following table. The iodine numbers, and the theoretical bromine values, calculated from the iodine numbers by multiplying by the ratio of the chemical equivalents of the two halogens, are also shown.

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[1] McIlhiney, P. G., The determination of bromine absorption of oils: Jour. Am. Chem. Soc., vol. 21, 1899, pp. 1084–1089.

Experimentally determined bromine numbers of a series of unsaturated naphthas compared with bromine numbers calculated from iodine numbers determined by the Hanus method.

Sample No.	Bromine value, determined by experiment	Bromine value, calculated from iodine value	Iodine number
1	162 9	165 6	263 0
2	103 5	91.3	141 8
3	78 4	80 3	127 4
4	72 8	72 2	114 6
5	60 3	55.0	87 1
6 .	49 7	41.8	66.4
7	35 6	29 4	46 7

Conclusions as to Bromine Method. -- The agreement between the determined and the calculated bromine numbers was reasonably good, but there was more difficulty in obtaining concordant duplicate results with the bromine than with the iodine method. Also more time was consumed in making the determinations by the bromine method and there seemed to be no advantages from its use. Greater rapidity has been claimed by some operators for the bromine method, but undoubtedly on the basis of comparison with one of the slower iodine methods, as for instance, the Hubl.

The question of the advantages and disadvantages of olefins in motor fuel is an important one. It is at present conceded (**Dean** and **Hill**) [1] that gasolines containing up to 12 per cent of "unsaturated" constituents are satisfactory motor fuel and that products containing a good deal in excess of 12 per cent "unsaturated" can be used without much trouble.

The importance of a standard method for determining the amount of olefins in gasoline is recognized by **Dean** and **Hill** who have made a careful study of the relative merits of four general methods, the iodine method of Hanus, the sulphuric acid absorption method, the "acid heat test" and the bromine absorption method. The conclusion is reached that the iodine method and the sulphuric absorption method are the only reliable ones and of these the sulphuric absorption method is the more "fool proof" of the two. The above investigators have standardized these methods in such a way that the presence of aromatic compounds is not deleterious when the proper conditions are observed.

[1] Bureau of Mines Technical Paper 181 (1917), p. 3.

Determination of Iodine Numbers by the Hanus Method.[1] — The **Hanus**[2] method of determining iodine numbers seems to be the most advantageous of any yet devised for this purpose. It is more rapid than the widely used **Hübl**[3] method and does not require the special reagents employed in the **Wijs**[4] method.

Preparation of Solutions. — The Hanus iodine solution is made by dissolving 13.2 grams of iodine and 3 c.c. of bromine in a liter of glacial acetic acid. This solution should be allowed to stand several days before using.

Sodium thiosulphate solution is prepared by dissolving approximately 25 grams of the crystallized salt ($Na_2S_2O_3.5H_2O$) in each liter of water.

Potassium dichromate solution is prepared by dissolving 3.8663 grams of very pure dry salt ($K_2Cr_2O_7$) in water and making up the volume to a liter. This is the basic standard solution for this method and must be prepared and preserved with great care. The quantity taken will liberate 10 grams of iodine from an acidified solution of potassium iodide.

Potassium iodide solution is made by dissolving one part by weight of the pure salt in nine parts of water.

Starch indicator solution may be prepared in various ways. The method of **Gooch**[5] is highly satisfactory; 5 grams of starch is mixed with a tiny bit (about 0.01 gram) of red mercuric iodide and rubbed to a smooth paste with cold water. This paste is poured into a liter of vigorously boiling water and stirred thoroughly, the boiling being continued for a minute or two. The solution is allowed to cool and settle; the clear portion is decanted into a bottle from which it is used. About 3 c.c. is used in each titration. If red mercuric iodide is not available the solution may be prepared without it, and when cold shaken with a few drops of chloroform, which acts as a preservative.

Standardization of Solutions. — Sodium thiosulphate solution is standardized against the potassium dichromate solution as follows: 25 c.c. of the latter, equivalent to 0.25 gram of iodine, is run from a pipette into a 200-c.c. Erlenmeyer flask containing about 12 c.c. of a 10 per cent solution of potassium iodide and 5 c.c. of ordinary concentrated, chemically pure, hydrochloric acid. The iodine thus liberated is titrated with sodium thiosulphate solution, the standard of the latter being recorded in grams of iodine equivalent to each cubic centimeter of the thiosulphate solution. The thiosulphate solution needs to be restandardized occasionally, as it changes slightly on standing.

[1] **Dean** and **Hill** *ibid.*, p. 6.

[2] **Hanus, J.,** Die Anwendung von Jodmonobromid bei der Analyse von Fetten und Oelen: Ztschr. Unters. Nahr. Genuss., vol 16, 1901, pp. 913–920. Hunt, F. W., A comparison of methods used to determine the iodine values of oils: Jour. Soc. Chem. Ind., vol. 21 1902, pp. 511–455. Smith, W. H., and Tuttle, J B., Iodine numbers of linseed and petroleum oils: Bureau of Standards Tech. Paper 37, 1914, pp. 1–14.

[3] **Hübl, --,** Eine allgemein anwendbare Methode zur Untersuchung der Fette; Dingler's Poly. Jour., Bd. 253, 1884 pp. 281–295; Jour. Soc. Chem. Ind., vol. 3, 1884, pp. 641–643.

[4] **Wijs, J. J. A.,** Zur Jod-Additionsmethode: Ber. Deut. Chem. Gesell., vol. 31, 1898, pp. 750–752

[5] Gooch, F. A. Methods in chemical analysis. New York, 1912, 536 pp.

The **Hanus** iodine solution is standardized daily in the regular course of making determinations by " running a blank " — that is, titrating a mixture made up like one of the unknown mixtures but without any gasoline.

Method of Determination. — The general scheme of procedure is as follows: Reaction mixtures are made up in the special glass-stoppered Erlenmeyer flasks sold for the purpose by chemical supply houses. The mixtures may be prepared at uniform intervals (five minutes is a convenient period) until thirty minutes have elapsed, when the first mixture is titrated. One of the factors that insures agreement of results is uniform time of reaction, and the 30-minute period should not be allowed to vary more than two or three minutes either way. Determinations may be run conveniently in series of six, as each mixture can be made up in a 5-minute period and the titration can be performed conveniently in that interval of time.

The procedure for a single sample is as follows: First, 10 c.c. of chloroform or carbon tetrachloride is measured into one of the glass-stoppered reaction flasks. The proper quantity of gasoline is then measured in, care being taken that there is no loss through evaporation. A convenient method of accomplishing this involves the use of a small capillary pipette made from glass tubing of about 1 mm. internal diameter and marked at intervals along its length. The volume from the pointed tip to each of the marks is determined by weighing the pipette first empty, and then filled with pure distilled water, measured at a temperature of 15° C. Different known quantities of gasoline, measured at the same temperature, can therefore be delivered from this instrument. The density of the gasoline should be known, measured for 15/15° C. The quantity used should be such that 10 to 30 per cent of the iodine used is absorbed. It is not always possible to hit on the right ratio between Hanus solution and gasoline at the first trial, but a second determination should always bring the quantities within the proper limits..

The capillary pipette, after being filled with the gasoline (at a temperature of 15° C.), is discharged with its tip held below the surface of the chloroform or carbon tetrachloride in the flask. The empty pipette is then partly washed by filling it once with the diluted gasoline mixture and letting the contents drain out. Washing is completed by filling once with pure solvent (chloroform or carbon tetrachloride) and draining again into the flask. This procedure avoids exposure of a large surface of pure gasoline to the air and reduces evaporation losses to a negligible quantity. The quantity of Hanus solution used by Dean and Hill was 10 c.c., and the quantities of gasoline between 0.04 and 0.20 gram.

The reaction mixture is allowed to stand for 30 minutes, preferably in the dark and never in direct sunlight. At the end of this time 25 c.c. of potassium iodide solution is poured in and 100 c.c. of distilled water added. The mixture is then titrated with the standardized sodium thiosulphate solution, care being taken to shake the mixture vigorously as soon as the yellow color fades in the aqueous layer. This precaution is to insure the removal of the iodine dissolved in the carbon tetrachloride or chloroform layer at the bottom of the flask. The starch indicator should not be added until after the yellow color of the iodine becomes faint. Warning of the approaching end of the titration is given by the color changing from greenish to blue. The titration is complete when the blue color just fades.

The iodine number is the percentage by weight of iodine absorbed and is calculated by the following procedure: The titer of the unknown mixture is subtracted from that of a blank, consisting of Hanus solution and solvent allowed to stand thirty minutes without any gasoline, and the difference in cubic centimeters of thiosulphate solution is multiplied by the weight of iodine equivalent to each cubic centimeter of the solution. The weight of iodine thus found is divided by the weight of gasoline taken, and the quotient is multiplied by 100, which gives the iodine number.

Method of Absorption by Sulphuric Acid.[1] — The method of absorption by sulphuric acid is similar in principle to the iodine absorption method, except that it involves measurement of a decrease in the quantity of the reagent. The method is more or less widely used, but generally without a knowledge of certain devices or methods of procedure that obviate experimental difficulties. When sulphuric acid is mixed with a highly unsaturated oil or gasoline there is a possibility that much heat may be developed and that gaseous reaction products may form with almost explosive violence. Some types of apparatus that are frequently used are not of proper design to minimize these difficulties and have the additional disadvantage of relatively high cost and fragility.

The procedure is simple, and it is said, has yielded satisfactory results with mixtures containing as much as 40 per cent of unsaturated hydrocarbons. The container employed is that described in the catalogues of chemical supply houses as the 6-inch, 9-gram, 40 per cent Babcock cream bottle. The neck of such a bottle is calibrated for the volume of 4.5 grams of butter fat, which is a little less than 5 c.c. An ordinary 5 c.c. pipette can be regraduated to deliver this quantity.

The gasoline to be tested is run into a clean, dry bottle, cooled for

[1] **Dean and Hill,** *ibid.,* p. 9.

a minute or two by immersing in ice water, and then 200 per cent by volume of ordinary concentrated sulphuric acid is poured in from a small graduate. Care should be taken that the acid runs quietly down the side of the bottle, instead of splashing onto the surface of the gasoline. A rubber stopper is then placed in the bottle and the contents are shaken, first slowly, then vigorously with a rotary motion for several minutes. The gasoline and the acid are separated by either one of the following two methods.

Gravity Separation. — Sulphuric acid is added to the contents of the bottle until the surface of the liquid is about level with the upper graduation mark on the neck of the bottle. The mixture is then set aside and allowed to stand overnight, when practically complete separation is effected.

Centrifugal Separation. — The stoppered bottle is placed in a suitable centrifuge and revolved for two or three minutes at a speed of 500 to 1000 r.p.m. Sufficient acid is then added to bring the level up to the lower graduation mark and the contents are again centrifuged to complete the separation. More acid is then added to bring the column to the upper graduation mark, after which the residual volume of gasoline is read.

Advantages of Method. — The results obtained have a possible error of 1 to 2 per cent, but within these limits seem to be thoroughly reliable. The iodine method, if properly applied, is undoubtedly the more accurate, and, unless a centrifuge is available, may be considered more rapid. However, it requires the operator to have considerable skill in the technique of iodimetry and yields results that may involve large errors if operative details are wrong.

The sulphuric acid method, on the other hand, is simple, reliable, although not highly accurate, and is more rapid than the iodimetric method if a centrifuge is available. If speed is measured in terms of the time required for the actual work of making up reaction mixtures, this method is more rapid even if overnight standing is employed, although a longer wait is then necessary before the results are available.

Tests to determine the olefin constituents of gasoline and kerosene are given by **J. Tausz** and **H. Wolf.**[1] The mercurization test [2] indicates the progress of the refining of mineral oils. It shows the presence of those unsaturated constituents which combine with alcoholic mercuric acetate at the ordinary temperature, but not of those which are only oxidized by the reagent. Since the first class of compounds is only present in very small proportion. it is best to determine both classes together.

[1] Z. angew. Chem. 1919, 32, 317–319; J. S. C. I. 1919, 889 A.
[2] J. S. C. I. 1919, 4 A.

For this purpose the oil is boiled with a dilute alcoholic solution of mercuric acetate, and the unaltered portion distilled in a current of steam and measured. The unsaturated hydrocarbons which have combined with the mercuric acetate are then liberated by means of hydrochloric acid, distilled with steam and measured. The determination is carried out in a flask with a side tube, which by inclining the flask can be connected with a reflux condenser cooled with alcohol and carbon dioxide for the boiling or with a vertical condenser and receiver similarly cooled for the distillation. The unavoidable loss is fairly constant and in the case of refined light petroleum spirit averaged 1.05 c.c. for 50 c.c. This value hence may be applied as a correction. For the analysis of petroleum spirit a solution of 30 grms. of mercuric acetate in 500 c.c. of water is placed in the flask, which is then connected with the reflux condenser, and 50 c.c. of the oil and 15 c.c. of alcohol are introduced into the flask through the condenser. After shaking, the flask is heated for 8 hours on a vigorously boiling water bath. The condenser is then inverted and attached to a burette terminating in the chilled receiver, and the hydrocarbons which have not reacted are distilled in a current of steam. The distillate is washed with 100 c.c. of dilute sodium hydroxide solution to remove acetic acid and then with 100 c.c. of sodium bisulphite solution to remove any aldehydes or ketones, the residual saturated hydrocarbons measured and the apparatus constant (i.e., 1.05) added to the amount. For the liberation of the combined unsaturated hydrocarbons strong hydrochloric acid is introduced into the flask, and the contents distilled as before in a current of steam. For the analysis of kerosene 30 grms. of mercuric acetate and 30 c.c. of alcohol are introduced into the flask, which is then shaken for five minutes before the introduction of 500 c.c. of water. The further procedure is as described above. Six samples of Galician light petroleum distillates contained from 1.0 to 4.2% (by vol.) of olefins, while a refined kerosene contained 3.3%. A crude American naphtha was found by Tausz and Wolf to contain 9.0% and two refined American petroleum spirits 3.2 and 1.2% respectively.

F. C. Ruff[1] removes unsaturated aliphatic hydrocarbons from a gasoline fraction containing an aromatic hydrocarbon, by heating with sulphuric acid containing not more than 1 per cent of nitric acid, that is, an amount insufficient materially to attack the aromatic compound.

Determination of Aromatic Hydrocarbons

An important consideration in motor fuels on the market at present is the content of aromatic hydrocarbons.

[1] J. S. C. I., 1918, 330 A; U. S. Patent 1,263,289, Apr. 16, 1918.

Rittmann, Twomey and **Egloff**[1] have evolved a specific gravity method for estimating and determining unsaturated hydrocarbons in the presence of aromatic hydrocarbons. Apparently the method is designed for the control of cracking processes when aromatic hydrocarbons are being produced from petroleum. It would, however, appear to be applicable also to the rapid estimation of benzene (benzol) in gasoline.

Successive redistillations are made through an efficient fractionating apparatus so as to give cuts at 95° C., 120° C. and 150° C. The specific gravity of these carefully obtained cuts is then made with an accuracy of one part in one thousand and, knowing accurately the specific gravity of the pure aromatic constituent (benzol, toluol or xylol as the case may be) and possessing a fairly accurate value for the specific gravity of the non-aromatic constituent, the amount of each in the fractions under examination may readily be determined by interpolation.

The assumption upon which this method is based is the gravity value assigned in each case to the non-aromatic constituents of the distillation cut. If, for example, unsaturated hydrocarbons have previously been removed by treatment with sulphuric acid in the cold, and if one possesses a fairly accurate knowledge of the composition of the non-aromatic saturated constituent, then a rough estimate of the proportion of aromatic and non-aromatic bodies in the mixture may be calculated from a specific gravity determination. The method is applied to separations of benzene, toluene and the xylenes from saturated aliphatics having boiling points in the neighborhood of the aromatic bodies mentioned.

For the chemical separation of aromatic and nonaromatic hydrocarbons, Rittman and his co-workers[2] prefer the nitration method, this being preceded by a removal of unsaturated open chain compounds.

(a) *Removal of Olefins.* — A 100-c.c. sample is measured into a 500-c.c. separatory funnel. To this is added 100 c.c. of sulphuric acid (sp. gr. 1.84). During the addition of the acid and the subsequent shaking for five minutes the mixture is cooled with ice water. A reddish-brown sludge forms which may readily be separated by centrifuging for fifteen minutes, although it does not settle with long-continued simple standing. The acid-sludge mixture is drawn off and the residual oil subjected to nitration according to the method of Lunge.[3]

[1] Met. and Chem. Engineering 1915 (13), 682, et seq.
[2] *Ibid.*, pp. 9 and 10.
[3] Coal Tar and Ammonia, Lunge, 4th edit. (1909), vol. II, p. 765.

(b) *Nitration.* — The procedure for nitration is briefly as follows: The sample is placed in a 500-c.c. flask equipped with a dropping funnel and a tube which acts as an air-cooled reflux condenser. Into the oil is run dropwise and with constant shaking a well-cooled mixture of 100 g. of nitric acid (sp. gr. 1.4) and 180 to 200 grams of sulphuric acid (sp. gr. 1.84). The flask is cooled during the addition by immersion in ice water. After the cessation of all tendency toward spontaneous heating of the mixture the flask and its contents are heated for two hours at a temperature of about 60° C. The escape of vapors is prevented by the use of an efficient reflux condenser. After cooling, the contents of the flask are transferred to a separatory funnel, allowed to settle and the lower acid layer drawn off. The latter is diluted with several times its bulk of water, and any oily liquid separating is added to the nitro-benzene.

The crude nitrobenzene is washed with water, very dilute caustic soda and again with water. It is dried and weighed, then distilled up to 150° C. and the distillate again treated with a large excess of the nitric-sulphuric acid mixture. Any liquid remaining undissolved in the acid is regarded as non-nitrifiable material.

Another nitration method of determining aromatic hydrocarbons in gasoline has been elaborated by **D. Florentin** and **H. Vandenberghe**.[1] To 20 c.c. of the gasoline, in a flask cooled in ice, nitric acid (specific gravity 1.5) is added, drop by drop, with shaking, until a brown tint is no longer produced, and the mixture is then left for fifteen minutes. The contents of the flask are poured into a large excess of water and neutralized with sodium hydroxide. By steam distillation small amounts of impurities arising from the oxidation of impurities in the gasoline are removed, and then the gasoline is decanted. The aqueous solution is extracted twice with light petroleum spirit, and the extracts are added to the decanted gasoline, this mixture then being made up to 100 c.c. with more light petroleum spirit. An aliquot portion is evaporated in a small glass dish in vacuo over sulphuric acid to constant weight (or very slight constant loss in weight), the residue being the nitro derivative. The weight of this, multiplied by 0.634 gives the weight of benzene.

Alternatively an aliquot portion may be heated with titanous chloride for two hours under a reflux condenser, and the residual titanous chloride titrated with a solution of ferric salt.[2] The second method is rapid and exact, and is preferable to the first when the gasoline contains any appreciable quantity of high boiling-point fractions. The examination of a number of samples of commercial motor

[1] Bull. Soc. Chim., 1920, 27. 204; J. S. C I., 1920, 325 A.

[2] J. S. C I., 1920, 224 A.

spirit shows that they contain appreciable quantities of benzene hydrocarbons, particularly toluene.

Aromatic hydrocarbons are removed from mineral oils by means of trioxymethylene-sulphuric acid according to **J. Tausz.**[1] The efficiency of **Nastjukoff's** formolite process [2] is increased by the use of trioxymethylene in place of formaldehyde solution. In the case of an oil volatile in steam, e.g., refined ligroin, 5000 c.c. is added to a solution of trioxymethylene (30 grms.) in sulphuric acid (100 grms.). The mixture is kept cool and well shaken for half an hour, after which ice (500 grms.) is added, and the oil distilled with steam. Salt may be added to the mixture before the addition of ice in order to protect the hydrocarbons from the sulphuric acid. Less volatile oils are first diluted with ten volumes of previously treated petroleum spirit. It is inadvisable to prolong the treatment, because a proportion of the oil, which increases with the duration of the reaction, is always lost. Thus 1.3.4-trimethylcyclohexane soon gave a coloration with the reagent, and after two days a yellow precipitate was obtained by successively adding ice and ammonia. Aromatic hydrocarbons can be detected in gaseous mixtures by the formation of a red precipitate on shaking with 1–2 c.c. of the reagent. The reaction is also shown by diolefins, such as methyl- and dimethyl-butadienes, which contain conjugated double bonds, but in the case of aromatic hydrocarbons is limited to those which contain a hydrogen atom in the nucleus. Thus, hexamethyl- and hexaethyl-benzenes do not respond to it.

Concerning the determination of aromatic hydrocarbons in gasoline **H. G. Colman** and **E. W. Yoeman** [3] state that on account of the increase in volume which occurs when aromatic and non-aromatic hydrocarbons are mixed, a correction must be made in calculating the volume percentage of aromatics from the specific gravity of gasoline fractions containing them as obtained before and after their removal by sulphonation. Since the expansion is a function of the particular aromatic hydrocarbons and its percentage in the mixture, it has been necessary to make a series of determinations for the preparation of graphs for benzene, and for toluene and xylene. Slight differences were found in gasolines of different origins (same boiling point), but these are of no consequence for the purpose in hand. The deviations of the calculated specific gravities from those observed are between 0.0 and 0.0045 for benzene and 0.0 and 0.0022 for toluene and xylene which are practically the same. If a_1, a_2 and a_3 are the respective specific gravities after removal of the benzene, toluene and xylene fractions as obtained in the method of **Thole** (Chem. Abs. 1919, 1013) and b_1, b_2, and b_3 the values before sulfonation, the true volume percentages are as follows: Benzene = 100 $((b_1 + k_1) - a_1) \div (0.855 - a_1)$: toluene = 100 $((b_2 + k_2) - a_2) \div (0.872 - a_2)$; xylene = 100 $((b_3 + k_3) - a_3 \div (0.868 - a_3)$, in which

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[1] J. S. C. I., Vol. 39, 1920, 147 A; J. prakt. Chem. 1919, 99, 276–280.

[2] J. S. C. I., 1904, 1082.

[3] Chem. Abs., 1919, 1922; J. S. C. I., 1919, 38, 82–83T.

k is the amount by which the specific gravity of a mixture of that percentage of the aromatic hydrocarbon and gasoline is lowered by the expansion which occurs on mixing them. The maxima in both graphs occur for mixtures of 50–60 per cent by volume of the aromatic hydrocarbon.

The critical temperature of solution of gasoline in aniline is used by **G. Chavanne** and **L. J. Simon** [1] to give the percentage of aromatic and of saturated cyclic hydrocarbons in petroleum spirit.[2] The critical temperature of solution in aniline is determined on the original spirit and on the spirit freed from aromatic hydrocarbons by nitration and washing with sulphuric acid. These two temperatures being represented by T_1 and T_2, the content of aromatic hydrocarbons is given by $Ar = k(T_2 - T_1)$. Assuming the values, T_a and T_c, for the critical temperatures of solution in aniline which would be given by the acyclic and the saturated cyclic hydrocarbons respectively, present in the spirit if isolated, then the content of the latter is given by $C = \dfrac{T_a - T_2}{T_a - T_c}$

$(100 - Ar)$. These formulae are only applicable where the percentage of aromatic hydrocarbons present is not greater than 15 or 20 and then $k = 1.18$. The values for T_a and T_c may be taken as $72°$ and $40°$ C. respectively. Where it is shown that ethylenic hydrocarbons are present to the extent of E per cent, expressed as amylene, then for T_1, in the formula, $T_1 + 0.4E$ should be written. In order to correct for traces of nitro-compounds left in the spirit after nitration, $T_2 + 0.2$ is used instead of T_2, and to correct for the slight departure from the law of additivity shown by the saturated cyclic hydrocarbons, $T_c - 0.5$ is used instead of T_c, i.e., the value becomes $39.5°$ instead of $40°$ C.

Using the above procedure for determining the critical temperature of solution (CTS) in aniline of hydrocarbons the observed CTS's of mixtures of acyclic hydrocarbons correspond to values calculated by the rule of mixtures. With mixtures of a different character, the agreement is not so good. A method of analysis of gasolines based upon this property of the mixtures has been devised, which consists in a fractional distillation of the mixture, separation of the aromatic hydrocarbons, determination of the CTS in aniline of each fraction and de-

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[1] Compt. rend. 1919, 169, 170 and 185; J. S. C. I. 1919, 619 A; Chem. Abs. 1920, 117.

[2] Using a method based on the critical temperature of solution in aniline the above investigators (Comptes rend. 1919, 169, 693–695; J. S. C. I. 1919, 619 A; 672 A; 889 A) have analyzed twenty-two samples of German aviation gasoline taken from a number of different aerodromes and find that they all closely approximate to the composition, aromatic hydrocarbons 10 per cent, saturated cyclic hydrocarbons 40 per cent, acyclic hydrocarbons 50 per cent.

termination of the CTS in aniline of each fraction freed of its aromatic hydrocarbon. The CTS in aniline of a mixture of acyclic hydrocarbons is lowered by the addition of an aromatic hydrocarbon in an amount proportional to the concentration of the aromatic hydrocarbon. The constant of proportionality for benzene is 1.14, for toluene 1.19, and for m-xylene 1.24. The proportionality is approximate, being a function of the concentration of the aromatic hydrocarbon and the composition and nature of the mixture of acyclic hydrocarbons, but it is sufficiently exact to prove useful. By a further distillation of each fraction and observation of the CTS of the fractions distilled to separate the saturated cyclic hydrocarbons, it is possible to determine the amount of saturated cyclic hydrocarbons. The accuracy obtainable depends largely upon the care employed in the fractionation of the mixtures.

The detection of aromatic hydrocarbons in light petroleum distillates is discussed by **J. Formanek, J. Knop** and **J. Korber.**[1] The presence of benzene in light petroleum may be detected by shaking a portion of the sample with a small amount of aniline color, e.g., " Blue B T " or " Violet R T " and filtering the mixture after two hours. If as little as two per cent of benzene is present, the liquid will be colored distinctly. By comparison with standards, this test may be rendered approximately quantitative. Ether, alcohol, carbon disulphide and chloroform interfere to a certain extent. Tests for the detection of turpentine oil in light petroleum, depending on the absorption of bromine or iodine are untrustworthy, since other unsaturated compounds are often present. The freezing point of a sample affords some indication of its composition. Pure benzene freezes at $+ 5.5°$ C. ($41.09°$ F.), a mixture of 25 per cent of benzene and 75 per cent of toluene and xylene at $- 10°$ to $- 20°$ C. ($+ 14$ to $- 4°$ F.) and technical xylene at $- 115°$ C. ($- 175°$ F.). The freezing point of light petroleum varies directly with the boiling point; a fraction boiling at 40–60° C. (104–140° F.) freezes at $- 198°$ C. ($- 324°$ F.) while a fraction boiling at 200–220° C. (392–428° F.) has a freezing point of $- 93°$ C. ($- 135°$ F.).

For a discussion of the dimethyl sulphate method of estimating aromatics in admixture with olefins and aliphatic hydrocarbons see **Rittman, Twomey** and **Egloff.**[2]

A method which depends on the different solubility of picric acid in paraffin and aromatic hydrocarbons respectively is used by **J. Tausz** and **S. Schnable**[3] for the detection of aromatic hydrocarbons. Pure

[1] Chem. Abs. 1918, 1596; Chem. Ztg., 1917 (41), 713–4, 730–1; J. Chem. Soc., 112, II, 581–2.

[2] Met. and Chem. Eng. 1915, 682, et seq.

[3] J. S. C I. 1919, 940 A; Chem. Zeit. 1919, 43, 726.

benzene dissolves about 10 per cent of its weight of picric acid, while
the latter is practically insoluble in hexane. About 50 grams of the
oil under examination is shaken for 10 minutes with 3 grams (or more
if necessary) of picric acid, filtered, 20 grams of the filtrate mixed with
30 c.c. of water and titrated with sodium hydroxide solution, using
phenolphthalein as indicator. The number of c.c. of N/1 alkali re-
quired to neutralize 100 grms. of the oil saturated with picric acid is
termed the picric acid value of the oil. For ordinary gasolines and
ligroins this value is usually less than 0.3. The following results were
obtained with a Rumanian gasoline, sp. gr. 0.7590, b. pt. $98° - 100°$ C.,
when mixed with varying quantities of benzene: —

Gasoline	Benzene (Benzol)	Picric acid value	Gasoline	Benzene (Benzol)	Picric acid value
%	%		%	%	
100	0	0.10	40	60	9.9
90	10	0 15	30	70	16.1
80	20	0 80	20	80	25.5
70	30	1.6	10	90	30 5
60	40	3 1	0	100	33.3
50	50	5.4			

In **Halphen's** method for the separation of low boiling aromatics
from petroleum spirit or oil [1] the unsaturated hydrocarbons are removed
with sulphuric acid and the remaining oil treated with fuming nitric
acid which converts the low boiling aromatic body into its mononitro
derivative. After the products of nitration are washed with water,
they are treated with a quantity of petroleum spirit sufficient to dis-
solve them. This solution is then shaken with sulphuric acid, where-
upon the nitroproduct is absorbed by the sulphuric acid and the increase
in volume of the latter is a measure of the amount of aromatic hydro-
carbon (e.g., benzene).

10 c.c. of petroleum spirit, from which olefins have been removed by shaking
with an equal volume of strong sulphuric acid, is placed in a flask closed with a stopper
pierced by two holes, through one of which passes the stem of a stoppered funnel
containing 10 c.c of fuming nitric acid, while a long tube passes through the other.
The acid is added four to five drops at a time, the flask being meanwhile continually
shaken and cooled in water, and the shaking is subsequently continued for 5 to 7
minutes. After the nitration is complete, 10 c.c. of water are introduced, little by
little through the funnel, while the flask is still kept cool, and then 40 c.c. of water,
which may be added in one volume, and the flask is well shaken and cooled, so that

[1] J. S. C. I. 1910, 1447; Les Matières Grasses, 1910 (3), 1987.

the nitrous vapors are absorbed. The products of the nitration are now transferred to a separating funnel, the flask being rinsed out with 10 c.c. of petroleum spirit (also purified by treatment with sulphuric acid), and the whole shaken for a few seconds and allowed to stand for 30 minutes. The aqueous layer and any insoluble oil are then drawn off and the petroleum spirit layer containing the nitro derivatives in solution is transferred to a stoppered graduated cylinder with a capacity of 30–35 c.c. where it is shaken with 5 c.c. of sulphuric acid (65.5° Bé). The cylinder is then allowed to stand for 30 minutes, after which the increase in volume of the acid is noted. This increase multiplied by 0.87 gives the *volume* of benzene in the sample taken. Since about 8 volumes of petroleum spirit are required to dissolve one volume of nitro benzene the sample under examination must not contain more than 20–25 per cent of benzene. When a greater proportion is present, the sample must be diluted with petroleum spirit.

The above method appears to be applicable to the analysis of " gasoline substitutes " where benzol is often used to adapt kerosene to the requirements of the present type of motor. It is not extremely accurate, however.

A method for the determination of benzene in benzol motor spirit is outlined by **Wa. Ostwald.**[1] The benzene can be separated from alcohol by shaking with water if the benzene content is at least 30 per cent. With a smaller content of benzene the addition of a known quantity of benzene is recommended. To 50 c.c. of the spirit in a 500 c.c. cylinder are added 10 to 20 c.c. pure benzene and then water to the mark. The separation of benzene follows without especial shaking. After 5 minutes the separated benzene is drawn off and the added benzene subtracted.

Another method for separating aromatic hydrocarbons from admixture with olefins and paraffins depends on the use of liquid sulphur dioxide.

S. E. Bowrey applies this method to the determination of toluene in crude petroleum. His procedure involves selecting the fraction boiling to 150° C. (302° F.), washing this with sulphuric acid to remove olefines and then subjecting the treated distillate to extraction with sulphur dioxide at − 35° C. (− 31° F.). It was found however that the extract contained paraffins as well as aromatic hydrocarbons. It was therefore necessary to employ specific gravity determinations in order to calculate the proportion of aromatic bodies.[2]

The sulphur dioxide method, although not fully developed, gives promise of being of the very greatest importance.

Moore, Morrell and **Egloff**[3] have determined quantitative relations in systems composed of liquid sulphur dioxide and typical specimens

[1] Der Motorfahrer, 15, 2–3; Chem. Zentr. 1918, II, 413; Chem. Abs. 1919, 3304.
[2] J. S. C. I. 1918, 455 A; J. Inst. Petroleum Tech. 1917 (3), 287–305.
[3] Chem. Met. Eng. 1918 (18), 396.

of hydrocarbons. Among other observations they have found that solutions of aromatic hydrocarbons in liquid sulphur dioxide possess the ability to dissolve paraffins, a capacity not possessed by sulphur dioxide alone. These investigators have separated xylene and octylene from a solution of these hydrocarbons in gasoline. The details of this separation are as follows.

Table 1 gives the result of adding equal volumes of sulphur dioxide to gasoline containing varying proportions of xylene and the olefin octylene The latter two, when present to an extent not exceeding 25 per cent of the volume of the oil, could be quite readily and almost completely removed as the refraction indices of the separated oils indicate. It is this separation which can be very usefully applied to the refining of American petroleums since the aromatics and olefins are consider-

Table 1. — *Paraffin-Aromatic-Olefin Mixture*

							Sp. Gr.	Index
(Paraffin) - Gasoline			.	.	.	. . . .	0.721	1.4008
(Aromatic) — Xylene					. .	.	0.880	1.4989
(Olefin) — Octylene			.		. . . .		0 724	1.4145

Temp. °C	% Paraffin in mixture	% Aromatic in mixture	% Olefin in mixture	% Mixture used	% SO₂ added	% Oil dissolved	Index of dissolved oil	Index of undissolved oil
− 18	95 0	3 3	1.7	50 0	50 0	4 0	1.4889	1.4010
− 18	90 0	6.7	3 3	50 0	50 0	9.5	1 4868	1.4013
− 18	85.0	10 0	5.0	50 0	50 0	12 0	1.4836	1.4065
− 18	80 0	13.3	6.7	50 0	50 0	17.5	1.4818	1.4087
− 18	75.0	16.7	8.3	50 0	50 0	31 5	1.452	1.4157
− 18	50 0	33 3	16.7	50 0	50.0	100.0	. . .	. . . . .

ably below the 25 per cent limit. Moreover, the olefins and aromatics are readily recovered from the sulphur dioxide, a fact which is in marked contrast with the refining losses due to the removal of unsaturated hydrocarbons with sulphuric acid.

As the percentage of aromatic and unsaturated compounds exceeded 25 per cent of the mixture, the solubility of the paraffins became more marked. With 50 per cent aromatic compounds and olefins present, the mixture was entirely miscible with the solvent.

This separation was checked up on crude unwashed Pennsylvania gasoline and kerosene. In each case the sulphur dioxide dissolved more than was removed by the sulphonation for olefins and nitration treatment for aromatic compounds. The index of the oil treated with sulphur dioxide showed much purer paraffin hydrocarbons remaining, while the dissolved olefins and aromatic compounds were recovered.

This therefore offers a method for separating aromatic oils of the solvent naphtha type, together with olefins from motor fuel containing such hydrocarbons, with the limitations indicated.

It is probable that Mexican and South American petroleum will become of constantly increasing importance and that a substantial part of our gasoline supplies will be obtained from these sources.

Suitable methods for determining hydroaromatic hydrocarbons therefore appear to be of importance, inasmuch as petroleum from the above mentioned sources often contains asphalt or asphalt yielding bodies; and gasoline and other distillates derived from such petroleums are quite apt to contain saturated and unsaturated cyclic hydrocarbons.

A method is described by **J. Tausz** and **N. von Putnoky** [1] by which cyclohexanes can be estimated in mixtures with araffins, depending on a measurement of the hydrogen liberated when a convenient quantity is circulated over a specially active palladium-black maintained at 270° to 300° C. (518° to 572° F.). Cyclohexanes are completely converted into benzenes in this way, but the paraffins themselves also produce a little hydrogen, an equilibrium with the olefin being established. The volume of hydrogen produced by the cyclohexanes, however, is nearly 20 times that developed by equal quantities of the paraffins under the same conditions, so that quantitative results are obtained with a fair degree of accuracy if there is more than 1 per cent of the cyclic hydrocarbons in the mixture. As an example of the application of the method, the proof of the presence of cyclohexane in a sample of hexane from American petroleum is given. 30 c.c. of synthetic n-hexane only gave 338 c.c. of hydrogen while 30 c.c. of the natural oil gave 446 c.c., corresponding to 2.4 per cent of cyclohexane in the sample. [2]

Viscosity

W. H. Herschel [3] is of the opinion that the usual method of judging the volatility or suitability of a gasoline by the density is only a rough approximation and that *fluidity*, which may be easily determined with a suitable viscosimeter, might prove, either alone or in conjunction with other tests, to be a preferable criterion. The Ubbelohde viscosimeter, it is said, designed primarily for use with kerosene, serves well enough for a commercial determination of the fluidity of gasoline. For purposes of calculation and comparison Herschel uses the " fluidity " value which is the reciprocal of the viscosity expressed in absolute units.

[1] J. S. C. I. 1920, 54 A; Ber. 1919, 52, 1573.
[2] See also J. Chem. Soc. 1920, ii, 61.
[3] Bureau of Standards Technological Paper No. 125, Viscosity of Gasoline. May 5, 1919, 18.

The Ubbelohde viscosimeter [1] is similar to the Engler in having a large, shallow container. It differs in the dimensions of the outlet tube, and in being provided with an overflow pipe to determine the initial level of the liquid, instead of gage points as in the Engler instrument. Viscosities are expressed in Ubbelohde degrees, obtained by dividing the time of discharge for the oil by the " water rate " or efflux time for 100 c.c. of water at 20° C. (68° F). Since water does not readily wet the surface of the container, especially after it has been previously filled with oil, the overflow cannot be used to bring the water level to the correct elevation. The following method is therefore employed in determining the water rate: A sufficient amount of alcohol is poured into the container so that a surplus runs out of the overflow. When the flow has ceased the container is emptied by pulling a skewer out of the top of the outlet tube (just as in starting the flow in an Engler instrument), and the volume of alcohol held in the container, below the level of the overflow, is measured. This same volume of water must be poured into the container when finding the water rate. If an excess of water is used, there is a tendency for it to cling to the overflow pipe, above the level of the liquid in the container, and thus to make the effective head too great.

Table 2 contains the standard dimensions of the Ubbelohde viscosimeter,[2] together with the dimensions of two instruments of the Bureau of Standards.

Table 2. — Dimensions of Ubbelohde Viscosimeters

Dimensions	Normal	Tolerance	Bureau of Standards instruments	
			No. 21	No. 22
	cm.	cm.	cm.	cm.
Inner diameter of outlet tube, at top	0.125	± 0.001	0.1311	0.1306
Inner diameter of outlet tube, at bottom	.125	± .001	.1282	.1277
Outside diameter of outlet tube, a' bottom, d_1	1.0	± .05	.9	.9
Length of outlet tube, l	3.0	± .01	2 934	3 068
Diameter of container, D	10.5	± .10	10.579	10 576
Outside diameter of overflow pipe, d_2	....		.67	.68
Initial head on bottom of outlet tube h_1	4.6	± .01	4.545	4.702
Average head, calculated	3.992		3.950	4 104
Water rate, seconds	200.	± 4.0	199.9	198.6
Capacity of container, cubic centimeter	.		132.	132.

It is also stated [3] that there is very little published information on the viscosity or fluidity of gasoline. It is noted that Sorel [4] gives information from which the

[1] Herschel, *ibid.*, p. 4.

[2] L. Ubbelohde, *loc. cit.*; also D. Holde, The Examination of Hydrocarbon Oils, translated by E. Mueller, 1915, p. 56.

[3] Herschel, *ibid.*, p. 16.

[4] E. Sorel, Carbureting and Combustion in Alcohol Engines, translated by Woodward and Preston, 1907, p. 165.

viscosity of fuels might be calculated, but all of them are more viscous than water. Brewer[1] quotes Sorel's table and gives additional data of his own, but his measurements were made with tubes of insufficient length. Table 3 shows fluidities of various gasolines as determined by the Ubbelohde viscosimeter and calculated by the equation[2]

$$\text{kinematic viscosity} = \frac{\text{viscosity in poises}}{\text{density, } g \text{ per cm.}^3} = 0.0000887\, t - \frac{1.438}{t}$$

where t is the time in seconds required for the discharge of one hundred cubic centimeters of liquid measured at 20° C. (68° F.). The gasolines are numbered in the order of their specific gravities. Fluidities calculated from times of discharge less than 155 seconds have been marked with an asterisk (*).

Table 3. — Fluidities of Gasolines at Various Temperatures

Gasoline No.	Specific gravity 15.6° C / 15.6° C.	Temperature					
		5° C.	15° C	25° C.	35° C.	45° C.	55° C.
1........	0.757	145	166	193	212	235	262
2........	.748	130	151	170	191	214	243
3........	.743	129	156	185	203	227	..
4........	.726	202	233	264	293	324	360*
5........	.722	189	219	244	278	308	342*
6........	.717	176	208	239	277	295	
7........	.716	197	217	256	289	321	311*
8........	.708	203	230	257	298	332	360*
9........	.702	233	261	296	321	358*	400*
10.......	.701	230	262	287	333	373*	398*
11.......	.699	233	269	306	335	372*	423*
12.......	.694	251	286	316	354*	387*	427*
13.......	.680	288	323	365*	413*	441*	475*
Kerosene....	.813	39	47	61	71	84	....

Gasolines Nos. 7 and 8 give an example of two fuels with practically the same gravity but greatly differing fluidity. Bingham has shown that the fluidity-vapor pressure curves of the aliphatic hydrocarbons are practically identical. This shows that the vapor pressure or volatility is determined by the fluidity for any of these pure substances, and suggested an investigation of the relation between fluidity and vapor pressure of gasolines which are mainly composed of these hydrocarbons. The experimental determination of the vapor pressure of gasolines has been found to yield widely discordant results, because the nonhomogeneity of the gasolines makes the observed vapor pressure extremely sensitive to slight changes in the experimental conditions.

[1] R. W. A. Brewer, Carburetion in Theory and Practice, p. 53, London, 1913.
[2] Herschel, *ibid.*, p. 11.

Figure 8 was plotted from data of Table 3, the fluidities of the aliphatic hydro-
carbons and of water being taken from the tables of Bingham and Harrison.[1] The
figure shows that kerosene has a lower fluidity or greater viscosity than water.
Ordinary commercial gasoline, as in samples Nos. 2 and 3, has about the same
fluidity as octane. The curve for sample No. 7 was omitted, it is noted, for the
sake of clearness as it would approximately coincide with that for heptane. Most
of the aviation gasolines, Nos. 4 and 8 to 12, are shown to be more fluid than heptane
and less fluid than hexane. Since the temperature-fluidity relation for these gaso-
lines is determined by a practically straight line, their fluidity would be determined
by specifying values at two temperatures.
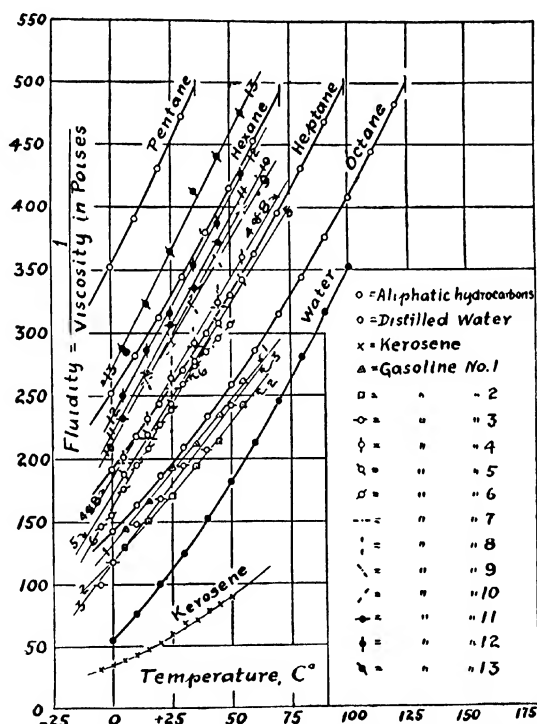
Fig. 8. — Temperature-fluidity curves of gasolines and other liquids.

It appears from Fig. 8 that fluidity might serve as an important criterion of the
quality or suitability of a gasoline where volatility is an important factor. It seems
probable that the fluidity is more closely connected with the volatility than is the
density. The test for fluidity, while it does not give the information obtained by a
fractional distillation in regard to the homogeneity or range of boiling points of the
fuel, is a comparatively simple test to make.

[1] E. C. Bingham and J. F. Harrison, Zeit. f. Physikalische Chemie, 66, 1909,
p. 12.

Vapor Pressure, Calorific Value and Sulphur Determination

Vapor Pressure. — This property is a direct measure of the " ease of starting " of a motor fuel. The comparative method of **Redwood** and **Thompson** is described by **H. Moore** [1] as follows:

" The apparatus consists of a thick-walled glass tube of small bore, about 30 in. long. The lower end of the tube is turned up and widens into a cylinder, about 6 in. long and 1 in. diameter, the upper end of which terminates in a short length of glass tube. The long tube is graduated in inches, divided into tenths, and the wide cylinder is provided with two marks, the lower corresponding with the zero of the scale and the upper being placed at nine tenths of the capacity of the cylinder above the lower mark. In use a short length of rubber tubing is wired to the top of the cylinder so as to cover it entirely, and project about $\frac{3}{4}$ in. above it. Mercury is poured into the cylinder up to the lower mark, and care is taken that the mercury thread in the tube is not broken. Enough of the liquid under test is poured into the cylinder to fill it well up to the upper mark and the apparatus is clamped vertically in a vessel of water at 50° F. After sufficient time has elapsed to allow of this temperature being attained by the apparatus and its contents, the level of the liquid is corrected, if necessary, and the rubber tubing is closed by a pinch cock screwed up very firmly just above the top of the glass tube, the open end of the india-rubber tube being further closed by a glass stopper. The whole apparatus is immersed above the top of the rubber tube in water at 50° F. The temperature of the water is raised very slowly by means of a rose burner and its temperature read by means of a thermometer immersed in it, unequal heating being avoided, as far as possible, by any form of mechanical stirrer. As the temperature of the water rises the height of the column of mercury in the capillary tube is read off at every 5° F. rise of temperature in the liquid, the heat being so regulated that this rise takes about 10 minutes, and is continued to 100° F."

K. Dieterich [2] has determined the rate of evaporation of several motor fuels, including " normal," light, medium and heavy benzene (petroleum spirit), motor benzol (90 per cent) and motor alcohol (95 per cent) and has plotted the results graphically. Good " normal benzene " gives a nearly straight, steeply falling, short curve. The higher the proportion of less volatile fractions present, the longer and more irregular the curve becomes, until it finally takes a nearly horizontal direction, as is shown in the curves for motor alcohol. The method of plotting the evaporation against the time is shown to be of great utility in the valuation of a motor fuel, a short, steep, straight curve indicating the best quality of fuel.

Redwood and **Lewes** [3] state that the determination of the calorific power of a highly volatile liquid with comparatively high vapor pressure

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[1] Liquid Fuels, D. Van Nostrand Co., 1918, p. 151.

[2] J. S. C. I. 1919, 244A; Petroleum, 1917, 12, 676–677; Chem. Zentr. 1919 190, 11, 31.

[3] Report on Hall Process of Manufacturing Motor Fuel, London, January 20, 1914.

in comparison with that of ordinary gasoline (e.g., 20.6 inches of mercury at 100° F. (37.7° C.) is attended with many difficulties and the use of the bomb calorimeter is unsatisfactory owing to the difficulty in preventing loss by escape of vapor during the weighing of the liquid and the violence of the explosion.

Vaporizing the spirit in any form of lamp or burner cannot be employed owing to the heavy fractions of high boiling point present. This difficulty is surmounted by atomizing the oil by pressure in a smaller reservoir mounted on a balance and burning the volatilized spray in a burner properly dimensioned to insure complete combustion in a Junker calorimeter.

G. Barsky [1] recommends the use of gelatin capsules in the determination of the fuel value of very volatile liquids in a bomb calorimeter. They are constructed of ordinary capsules by turning in the caps so that the latter fit the menisci when the capsules are filled; all air is thus excluded. The igniting wire is wound round the capsule.

For estimating sulphur in motor fuel **W. A. Bradbury** and **F. Owen** [2] use a modified Referee apparatus in which the combustion gases are passed through a column of beads that are moistened at intervals with reagent. Bradbury and Owen displace the spirit lamp by a carburetor in which air is carburetted by being blown through the motor spirits. Extra air may be supplied to the vapors. A small reservoir of pure gasoline is supplied to a pilot flame while the apparatus is being assembled and another of turpentine is connected to the carburetting tube to be used for sweeping out the last traces of spirit from the carburetor. The latter is placed in a water bath, and may be heated when necessary. The apparatus is claimed to give very concordant results.

Lomax [3] has also reviewed methods of determining the sulphur content of motor spirit. He commends a modification by Esling of the combustion method, in which the motor spirit, after admixture with alcohol, is burnt from a small wick lamp in a current of air. Such a method is undoubtedly more trustworthy, it is said, for motor spirits of tolerably low sulphur content than determination of the sulphur through the products of combustion of the spirit in the bomb calorimeter.

The " Doctor " Test. — The United States Bureau of Mines [4] has formulated this test as follows:

Obtain pure flowers of sulphur and prepare the sodium plumbite or doctor solution. For the latter, dissolve approximately 125 grams of sodium hydroxide

[1] J. S. C. I., 1920, 147 A; J. Ind. Eng. Chem. 1920, 12, 77.
[2] Chem. Abs. 1914, 3853; Chem. News, 110, 163–5.
[3] J. Inst. Petrol. Tech. 1917 (4), 19; J. S. C. I. 1918, 116A.
[4] Dean, Bureau of Mines Bulletin 214 (1919).

(NaOH) in a liter of distilled water, add 60 to 70 grams of litharge (PbO) and shake vigorously for 15 to 30 minutes, or let it stand with occasional shaking for a day. Allow it to settle and pour or siphon off the clear liquid. If the solution fails to settle properly it may be filtered through a mat of asbestos. The solution must be kept in a bottle closed tightly with a cork stopper.

In making the test shake together vigorously two volumes of gasoline and one volume of the doctor solution (10 c.c. and 5 c.c. are convenient quantities) in a test tube; or, if preferred, an oil sample bottle may be used with correspondingly larger quantities. After shaking together for about 15 seconds, add a small pinch of flowers of sulphur, shake the tube again for 15 seconds and allow the contents to settle. The quantity of sulphur used shall be such that practically all of it floats on the surface, separating the gasoline from the doctor solution.

If the gasoline is discolored, or if the sulphur film is so dark that its yellow color is noticeably masked, the test shall be reported as positive and the gasoline condemned as " sour." If the liquid remains unchanged in color and if the sulphur film is bright yellow or only slightly discolored with gray, or flecked with black, the test shall be reported negative and the gasoline considered " sweet."

Distillation

Dean [1] proposes the following method:

Distillation Method and Apparatus. — The distillation method recommended is approximately that adopted by Subcommittee XI of Committee D1 of the American Society for Testing Materials.[2]

The two noticeable points of variation are the method of reading temperatures against fixed percentage points and the use of a thermometer of lower range. The method of the society is proposed for the analysis of turpentine substitutes which are petroleum products of higher boiling range than gasoline.

The apparatus used should be as follows: The particular form employed is represented in Fig. 9 and differs somewhat in appearance, though not in the essential details, from that generally supplied in the market for this test.

Flask. — The flask used shall be the standard 100-c.c. Engler flask, described in the various textbooks on petroleum. Dimensions (outside) are as follows:

Dimensions of Flask

Dimensions	Cm.	Inches
Diameter of bulb	6.5	2.56
Diameter of neck	1.6	0.63
Length of neck	15.0	5.91
Length of vapor tube	10.0	3.94
Diameter of vapor tube	0.6	0.24

[1] Bureau of Mines Bulletin 214 (1919).

[2] American Society for Testing Materials, Year Book for 1915, pp. 568–569; or pt. 1, Committee Reports, 1916, vol. 16, pp. 518–521.

Position of vapor tube, 9 cm. (3.55 inches) above the surface of the gasoline when the flask contains its charge of 100 c.c. The tube is approximately in the middle of the neck.

The flask shall be supported on a ring of asbestos having a circular opening $1\frac{1}{4}$ inches in diameter; this means that only this limited portion of the flask is to be heated. The use of wire gauze or a sand bath is not approved.

Condenser. — The condenser shall consist of a thin-walled tube of metal (brass or copper) approximately one-half inch internal diameter
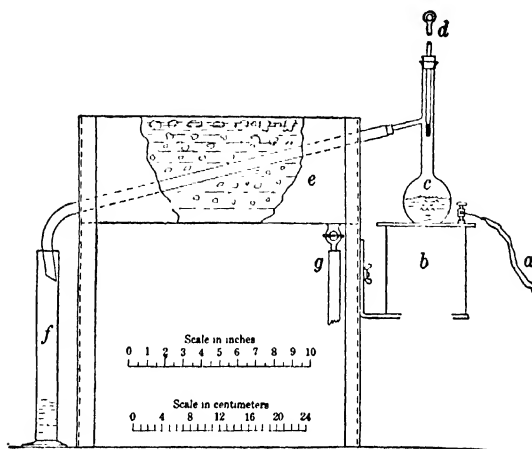
Fig. 9. — Apparatus for distillation test of gasoline. (*a*) Wires connecting with electric mains through a suitable rheostat. (*b*) Electric heater. (*c*) Engler distillation flask filled with charge of gasoline partly distilled. (*d*) Thermometer. (*e*) Condenser, with trough filled with ice and water. (*f*) Receiving graduate. (*g*) Cock for draining condenser trough.

and 22 inches long. It shall be set at an angle of 75 degrees from the perpendicular and shall be surrounded with a cooling jacket of the trough type. The lower end of the condenser shall be cut off at an acute angle and shall be curved down for a length of 3 inches. The condenser jacket shall be 15 inches long.

Thermometer. — The thermometer should be an accurate nitrogen-filled instrument with a short bulb (length 10 to 15 mm., 0.39 to 0.59 inch) and with the mark for 35° C. (95° F.) at a distance between 100 and 120 mm. (3.94 to 4.75 inches) from the top of the bulb. The thermometer should be scaled for total immersion.

Procedure and Details of Manipulation in Conducting Distillations. [1] — 1. If an electric heater is used it is started first.

2. The condenser box is filled with water containing a liberal proportion of cracked ice.

3. The charge of gasoline is measured into the Engler flask from a 100 c.c. graduate. This graduate is used as a receiver for distillate without any drying. This procedure eliminates errors due to incorrect scaling of graduates and also avoids the creation of an apparent distillation loss due to the impossibility of draining the gasoline entirely from the graduate.

4. The above-mentioned graduate is placed under the lower end of the condenser tube so that the latter extends downward below the top of the graduate at least 1 inch. The condenser tube should be so shaped and bent that the tip can touch the wall of the graduate on the side adjacent to the condenser box. This detail permits distillates to run down the side of the graduate and avoids disturbance of the meniscus caused by the falling of drops. The graduate is moved occasionally to permit the operator to ascertain that the speed of distillation is right, as indicated by the rate at which drops fall. The proper rate is from 4 c.c. to 5 c.c. per minute, which is approximately two drops a second. The top of the graduate is covered, preferably by several thicknesses of filter paper, the condenser tube passing through a snugly fitting opening. This minimizes evaporation losses due to circulation of air through the graduate and also excludes any water that may drip down the outside of the condenser tube on account of condensation on the ice-cooled condenser box.

5. A "boiling stone" (a bit of unglazed porcelain or other porous material) is dropped into the gasoline in the Engler flask. The thermometer, equipped with a well-fitted cork and with its bulb covered with a thin film of absorbent cotton (preferably the long-fibered variety sold for surgical dressings), is fitted into the flask with the thermometer bulb just below the lower level of the side neck opening. The flask is connected with the condenser tube.

6. Heat is applied cautiously and the gasoline brought to its boiling point. In case it is desired to record the initial boiling point the thermometer is read when the first drop falls from the end of the condenser tube into the graduate. The amount of heat is then increased so that the distillation proceeds at a rate of from 4 c.c. to 5 c.c. per minute. The thermometer is read as each of the selected percentage marks is reached. In case maximum boiling point or dry point (one definition of end point) is to be measured, the heating is continued

[1] Dean, *loc. cit.*

after the flask bottom has boiled dry until the column of mercury reaches a maximum and then starts to recede consistently.

7. Distillation loss is determined as follows: The condenser tube is allowed to drain for at least five minutes after heat is shut off, and a final reading taken of the quantity of distillate collected in the receiving graduate. The distillation flask is removed from the condenser and thoroughly cooled as soon as it can be handled. This can be accomplished by using first an air bath and then immersing the bulb of the flask in the ice-water mixture in the condenser trough. The condensed residue is poured into a small graduate or graduated test tube and its volume measured. The sum of its volume and the volume collected in the receiving graduate, subtracted from 100 c.c., gives the figure for distillation loss. In case this loss exceeds 2 per cent, a check distillation should be run to ascertain whether such loss is due to the presence of highly volatile constituents or to failure to condense the lighter fractions on account of too strong heating at the beginning of the distillation.

A constant temperature still-head for light oil fractionation recommended by **F. M. Washburn** [1] consists of two essential parts, namely, a Hempel column and a constant temperature still head of the type suggested by **F. A. Brown.** [2] This still head is a spiral of about 6 inches diameter made from 12 feet of $\frac{3}{8}$ inch iron tube; it is surrounded by an oil-bath, which is provided with a stirrer and maintained at the required temperature by a coil of resistance wire, thermo-regulator, relay, etc. The lower end of the spiral is connected with the side-tube of the Hempel column, while the upper end is fitted with a thermometer pocket and a side-tube leading to an ordinary condenser.

GASOLINE SPECIFICATIONS

Distillation and analysis of over 800 samples, covering practically all types of gasoline produced and sold in the different parts of the United States, reveals according to the Bureau of Mines [3] that only 26.9 per cent pass the requirements of the present specification which, the report says, does not conform to good refinery practice in that there is too much difference between the 90 per cent point and the dry point. Also, both these points are a little too low compared to the other points in the specification. Rather than adopt the suggested plan of having two specifications, one (grade B) somewhat more rigid

[1] J. Ind. Eng. Chem. 1920, 12, 73–77; J. Chem. Soc. 1920, Abs. 117–118, ii, 88.

[2] Trans. Chem. Soc. 1880, 37, 49.

[3] Oil Paint and Drug Reporter, Sept. 29, 1919, 33.

than the present, and one (grade R) decidedly less rigid, the Bureau is in favor of adopting the single specification plan known as grade M, which raises the 90 per cent point in distillation from 180° C. to 190 degrees and the end point from 220 degrees to 225 degrees, thereby remedying the two faults referred to above as existing in the present specification.

Matter of Readjustment. — It is stated in the report that the change from the present specification to grade M will be more in the nature of a readjustment than a radical change, and it is estimated that its adoption at the present time will obviate necessity of further change for at least two, or possibly three, years; nor is it likely to cause any restriction of output for some time to come.

The report in full follows:

Report of Committee. — The Committee on Standardization of Specifications for Petroleum Products, created by order of the president, dated July 31, 1918, requested the Bureau of Mines to consider the revision of the specification for motor gasoline, as printed on page 9 of Bulletin No. 1 of the report of the above committee issued by the Fuel Administration in October, 1918. The specification is as follows:

Specification for Motor Gasoline

As Adopted by the Committee on Standardization of Petroleum Specifications, October 2, 1918

Quality. — Gasoline to be high grade, refined and free from water and all impurities, and shall have a vapor tension not greater than 10 pounds per square inch at 100° F. temperature, the same to be determined in accordance with the current "Rules and regulations for the transportation of explosives and other dangerous articles by freight," paragraph 1824 (k), as issued by the Interstate Commerce Commission.

Inspection and Tests

Inspection. — Before acceptance the gasoline will be inspected. Samples of each lot will be taken at random. These samples immediately after drawing will be retained in a clean, absolutely tight, closed vessel and a sample for test taken from the mixture in this vessel directly into the test vessel.

Test. — One hundred cubic centimeters will be taken as a test sample. The apparatus and method of conducting the distillation test shall be that described in Bureau of Mines Technical Paper No. 166 " Motor Gasoline."

(a) Boiling point must not be higher than 60° C. (140° F.).

(b) Twenty per cent of the sample must distill below 105° C. (221° F.).

(c) Forty-five per cent must distill below 135° C. (275° F.).

(d) Ninety per cent must distill below 180° C. (356° F.).

(e) The end or dry point of distillation must not be higher than 220° C. (428° F.).

(f) Not less than 95 per cent of the liquid will be recovered from the distillation.

To Cover Federal Purchases

This specification was drafted to cover Federal purchases of motor gasoline, both for domestic and for military uses, and represented a grade equivalent to a large proportion of the motor gasoline marketed in the calendar years 1917 and 1918. It has in addition been included in several State and municipal legislative acts regulating the sale and quality of gasoline. The specification has recently been criticized as too rigid for present refining and marketing practice, and it has been claimed that if all gasoline produced conformed to its requirements, the nation's supply of motor fuel would be materially reduced.

To obtain information on this subject the Bureau of Mines has made a survey of the gasoline marketed throughout the entire country and has collected through its agents a total of over 800 samples, covering practically all the types of gasoline produced and sold. Samples have been obtained in all the states of the country and have included the production of all refineries of sufficient size to be of importance in the aggregate supply. The data collected in this survey are believed to be the most comprehensive now available with regard to the grades and quality of motor fuel.

The figures obtained through laboratory analysis of these samples have been studied to ascertain what proportion of the total number satisfied each requirement of the specification and what proportion satisfied all requirements. The following table shows results of this study:

Present Spec fication

	First drop	20 %	45 %	90 %	Dry
Specification mark °C.	60	105	135	180	220
Maximum distillation temperature, °F....	140	221	275	356	428
Per cent of samples tested satisfying each limit requirement....	81.7	89.0	89.7	37.2	50.1

The limit on the temperature below which 90 per cent of the gasoline distilled was the most rigid and the number of samples meeting this requirement was notably less than that meeting any of the other points. As all samples satisfying the 90 per cent requirement did not satisfy all other requirements, it was found that the number passing the requirements for all the distillation marks was only 26.9 per cent of the total.

Two Lines of Action Proposed

Two lines of action were then proposed. First, replacing the present specification by one (Grade M) that would allow approximately half the samples included in the present survey to pass, and that would not reduce the present supply if all gasolines were made under one specification. Second, drafting specifications for two grades of gasoline, one (Grade B) slightly more volatile than that represented by the present specification, the other (Grade R) covering a notably less volatile grade. The following specifications were drafted and studied in the same manner as before. The following tabulation shows the number of samples in the series collected by the Bureau of Mines satisfying each limit:

Government Standard Motor Gasoline. Grade M

Limit.	Init.	20 %	50 %	90 %	Dry
Degrees C.	60	105	140	190	225
Degrees F.	140	221	284	374	437
Per cent passing limit	81.7	89.0	90.2	67.8	74.6
Percentage passing all requirements . 46.0					

Government Standard Motor Gasoline. Grade B

Limit.	Init.	20 %	50 %	90 %	Dry
Degrees C.	60	105	140	180	215
Degrees F.	140	221	284	356	419
Per cent passing limit	81.7	89.0	90.2	37.2	45.7
Percentage passing all requirements . 25.2					

Government Standard Motor Gasoline. Grade R

Limit	Init.	20 %	50 %	90 %	Dry
Degrees C.	65	110	150	210	235
Degrees F.	149	230	302	410	455
Per cent passing limit	90.4	97.5	86.2	91.9	89.2
Percentage passing all requirements . 75.9					

Percentage Limit Changes

In drawing up the specifications, two changes of percentage limits were considered:

1. The 45 per cent point. It is customary in making laboratory distillations to read the temperature as each 10 per cent distills off, and for that reason the introduction of a requirement for 45 per cent means an additional reading and does not have any advantage over a 50 per cent requirement. Accordingly, the intermediate requirement has been changed from a temperature limit below which 45 per cent must distill to a temperature limit below which 50 per cent must distil. A study of the figures obtained by the analysis of over 800 samples shows that a requirement of 50 per cent distilling below 140° C. (284° F.) is equivalent to 135° C. (275° F.) for 45 per cent and the new specifications have been drawn up on this basis.

2. The initial point. Owing to difficulty in obtaining check results on initial boiling points it has been suggested that this point be left out of the specification and as a means of controlling the content of highly volatile material a temperature limit be fixed below which five per cent must distill off. From a laboratory standpoint the five per cent requirement is preferable, for it is difficult for different laboratories and different operators to check initial boiling points. However, the petroleum industry is familiar with initial boiling points and to specify a new requirement would cause considerable confusion; also, it would be possible for products containing high percentages of benzol to satisfy the requirement for the five per cent point, although such products might have very little material boiling below 75° C. and would not be satisfactory for use in cold weather.

Difficulty in Check Results

Since the chief difficulty in getting check results in initial boiling point temperatures is caused by using various rates of heating, it is believed that standardizing the interval of time between the first application of heat to the flask and the time the first drop leaves the condenser, within rather narrow limits, will enable different operators to check initial boiling point temperatures. The standard method for the distillation of gasoline fixes the rate of heating after the distillation is started, but does not specify a definite length of time of obtaining the first drop, and as a result it is possible to vary as much as 5° C. on first-drop temperatures, depending entirely on the rate of heating.

The Bureau of Mines is at present conducting experiments on the effect of the rate of heating on the temperatures of the initial boiling points, and will establish a standard method of determining this point, placing an upper or a lower time limit on the interval between the first application of heat and the time the first drop leaves the condenser.

It is believed that when this method has been standardized a speci-
fication requirement for an initial boiling point will be satisfactory and
a 5 per cent requirement will not be necessary.

Loss in Production

The next question taken up was the actual loss in production under
each of the four specifications, assuming that all of the high grade
gasoline now produced be kept as at present, and all the gasolines
below the specifications be brought up to the specification requirements.
The following results were obtained by a study of each of the 836 analy-
ses, and the loss of production for each sample which did not pass the
specification in question was determined. These losses were totaled,
and the average loss of production determined for the specification.
On this basis, Grade B would produce a loss of production of 4.51 per
cent, the present specification a loss of 3.54 per cent, Grade M a loss
of production of 2.25 per cent, and Grade R a loss of production of
.56 per cent. To check these figures a sample of low-grade gasoline
was redistilled in a Hempel still, so that the resulting distillates would
pass each of the specifications in turn. It was found that the calculated
figures were very close to those obtained in the laboratory. As it is
known that refinery practice cannot equal laboratory efficiency, a
refinery loss equal to the calculated loss was allowed.

Study of 836 Analyses

On studying the 836 analyses it was found that the samples ranged
in volatility from some that would almost pass the specification for
" domestic aviation " gasoline to some that would not pass a speci-
fication even more lenient than Grade R. This is due to three things,
first, to variation in the crude oils, second, to variations in refinery
methods, and third, to faulty distribution of casinghead gasoline and
of the various gasoline fractions, some parts of the country having an
excess of light fractions, and others having an excess of heavy ones.
This condition would be remedied if all gasolines could be blended to
an uniform standard. It is commercially possible to improve refinery
practice in this regard, but even under the best conditions there would
be some gasoline that would fail to pass any reasonable specification.
In some cases there would be too much of the more volatile fractions,
whereas in others there would be not enough. It is commercially
impossible to get an entirely even distribution of all the fractions.
If these gasolines were excluded, as would happen if the specification
was rigidly enforced, a certain percentage of loss of production would

result. This loss has been estimated as equal to the refinery loss. The resulting combined losses of production are as follows:

Losses in Production

Domestic production, 1918, motor gasoline, 70,000,000 barrels

	Loss, Barrels
Grade B = 4.51 × 3 = 13.53 per cent................	9,471,000
Present grade = 3.54 × 3 = 10.62 per cent...........	7,434,000
Grade M = 2.25 × 3 = 6.75 per cent................	4,725,000
Grade R = 0.56 × 3 = 1.18 per cent................	826,000

In the above work it was assumed that only the low-grade gasolines were to be changed. Obviously, if all the gasolines, both more and less volatile, were to be brought to the specification, the losses of production would be less. Accordingly, the average results of all the 836 samples were computed, first, as a straight average, second, by refining companies, allowing each of the large companies its proper weight according to its output, and third, by consumption, each State being allowed its proper weight according to the percentage of automobile registrations. These three averages follow:

Distillation Results, 836 Samples

	First drop	20 %	50 %	90 %	Dry
Straight average.....	51.6	95.0	127.2	183.2	217.0
Weighted by production	48.1	95.6	128.8	185.9	216.6
Weighted by consumption...... ..	50.6	95.3	125.2	184.1	215.3
Average of 3 methods....... .	50.1	95.3	127.1	184.4	216.3
Maximum deviation from average	2.0	.3	1.9	1.5	1.0

Little Average Difference

It will be noted that there is very little difference in these three averages, so that the average of the three has been taken as a basis for computing losses or gains. Assuming that the three-method average represents the quality of the gasoline sold in the United States, and that all samples are brought to the specification, then

Grade B will produce a loss of 1.81 per cent.
Present grade will produce a loss of 1.81 per cent.
Grade M will produce a gain of 2.30 per cent.
Grade R will produce a gain of 10.50 per cent.
Assuming refinery and distribution losses as before:
Grade B = 1.81 × 3 = 5.43 per cent loss.
Present grade = 1.81 × 3 = 5.43 per cent loss.
Grade M = 2.30 × ⅓ = .77 per cent gain.
Grade R = 10.50 × ⅓ = 3.50 per cent gain.

Specification M represents present refinery practice much more nearly than any of the other specifications. If all the gasolines produced, both more and less volatile, were brought to this standard, there would be a net gain of approximately 1 per cent in production. However, the present specification is stated to be such as to afford enough gasoline for the present needs of the United States, although the theoretical loss, if this specification were rigidly adopted, would be approximately 5 per cent. Consequently, if specification M is adopted, and the same ratio of refinery practice to the theoretical practice is continued, the gain in production would be about 6 per cent. Inasmuch as the present production of gasoline appears to be sufficient at the present time, and allowance being made for the probable increase of production of high grade crude oil in the Texas field, for increased importations from Mexico and increased cracked gasoline, it is estimated that if specification M is adopted at the present time no change in the specification will be required for at least two years, and possibly not for three years.

Matter of Readjustment

The change from the present specification to grade " M " will be more in the nature of a readjustment than a radical change. The present specification does not conform to good refinery practice in that there is too much difference between the 90 per cent point and the dry point. Also, both these points are a little too low compared to the other points in the specification. This is very plainly brought out by drawing distillation curves of the present specification and of the average results of the 836 analyses. Raising the 90 per cent point from 180° C. to 190° and the end point from 220° to 225°, remedies both of these faults and balances the specification. Consequently, if the present plan of a single specification is to be retained, grade " M " should be adopted. The alternative plan is to have two specifications; one somewhat more rigid than the present and one decidedly less rigid. These are the " B " and " R " grades described above. Grade " B " would be like the present grade, but 5 per cent lower in end point. This change would tend to make a better balanced specification. Grade " R " would be less rigid all through the distillation range and would approximate in quality a large amount of gasoline now used and sold in the Middle West. The arguments in favor of the two specifications plan are that it would allow of conservation of the higher grade material for military use, winter use, and other special purposes, and that it would allow of a large increase in the production of gasoline. Inasmuch as there is already one high grade gasoline now available, namely,

" domestic aviation," it seems necessary to specify a grade any better than the present grade for the special uses mentioned above. And, as already stated, the adoption of grade " M " is not likely to cause any restriction of output for some time to come. The arguments against the two specifications plan are that it adds confusion to the gasoline market, and that a number of dealers would find it necessary to carry two grades, with consequent increase of storage capacity. Considering the matter from all sides, the Bureau of Mines is in favor of adopting the single specification plan (grade " M ").

Lack of Uniformity

In conclusion one thing more can be said. There is at present a great lack of uniformity in refining and marketing practice as regards quality. This is evident from a study of the figures presented. For instance, only 46 per cent of the samples tested passed the " M " specification at all points, and yet if this specification was rigidly enforced and all the motor gasoline produced in the United States was blended into a uniform product, it would be well under all the limits. This shows that the 46 per cent of samples that passed are enough more volatile than the specification to more than balance the 54 per cent that are less volatile, and a detailed study of the individual samples confirms this.

This situation should be corrected. If the gasolines of the United States are made more nearly uniform, the consumer can get greater economy in actual use, and thus tend to conserve the available supply, and the use of one specification more rigidly enforced would be one method of accomplishing this result.

CHAPTER III

REFINERY PRACTICE

I. The Treatment of Paraffin and Semi-Paraffin Crudes.

The production of gasoline from petroleum is a subject that has engaged the attention of thousands of highly trained specialists ever since gasoline came into prominence in connection with the internal combustion engine. Practically every phase of the subject has been probed in attempts to find various ways and means for recovery of the light hydrocarbons naturally present in the crude petroleum and for the breaking down of the heavier hydrocarbons except those which are in themselves in as much or greater demand than gasoline and which it is not economical to decompose. Some of the methods for accomplishing the same end differ largely in detail rather than in principle; other methods differ considerably among themselves in principle as well as in the details of execution. As will be further described in the following chapters a large number of methods both for ordinary distilling, as well as for heat decomposition or cracking, involve passing petroleum or its fractions through special reaction chambers which often involve tubes or retorts or a combination of the two avoiding as much as possible the use of large containers for the oil which is being distilled or decomposed. There are, it may be said, at least two large classes into which may be divided methods for separating petroleum into its fractions and for decomposing some of the heavier fractions to yield lighter oils, namely tube and still processes. In this country, at least, the still processes predominate very largely.

The demand for gasoline has long since exceeded the available natural supply contained in the crude oil and an important part of refinery practice at the present time consists in augmenting the natural supply of light hydrocarbons by processes of decomposing the heavier oils by heat treatment and thereby obtaining increased quantities of motor fuel. Nevertheless the separation of the light hydrocarbons naturally contained in the crude oil still retains a very large and important position in refinery practice. This phase of the subject may therefore logically be taken up first.

In this branch, refinery engineering has resulted in many important improvements over the crude processes which were in vogue years

ago. It has always been a rather difficult problem to recover from the crude oil the hydrocarbons which are desired in the condition and proportions as they exist in the natural petroleum. This is due of course to the fact that there is an almost imperceptible gradient in properties, as regards any series of hydrocarbons, as we pass from the lower members to the higher members of that series. Indeed it is not known to the authors that any fraction of petroleum has ever been separated on a large scale into its ultimate fractions. This gradation is especially the case with the higher boiling bodies. The endeavor has always been so to conduct the distillation as to avoid in any fraction the presence of hydrocarbons whose properties place them in the fraction next higher or next lower. Nevertheless it appears almost impossible as the operation is carried out at the present time to effect this object in a single distillation. The contemporary methods for separating crude petroleum into those parts which are demanded by the oil trade (and which are not at all ultimate separations) takes place today rather by fractional condensation than by fractional distillation although the result is really a combination of the two effects. That is, the practice is to vaporize as large an amount of oil as possible in as short a time as is practical, pass the vapors through large air condensers, where, by means of tubular coolers, a large surface is exposed to the cooling action of the air and to collect condensates of varying gravities at different parts of the air condensers, whose cooling and separating action is supplemented by water cooled condensers. This method is the result of a series of efforts extending through a long period of time to effect in one distillation as nearly complete as possible a separation of the fractions of the crude oil in such a way that these fractions will require as small an amount of redistillation as possible. It is also the result of a demand for large outputs within as short a space of time as possible, and as carried into effect today serves this purpose, at least to a large extent. It is a very important improvement over older methods but, nevertheless, it must be said it is only a very crude separation and has to be supplemented by subsequent operations.

The essential features of a crude oil distillation may therefore be considered to be the action of the fractionating air condensers, or " towers " as they are called in refineries.

Throughout refinery practice it is interesting to note how often the analogy crops out between water and steam boilers, on the one hand, and on the other hand the stills, condensers and heat exchangers in the petroleum distillation industry. The units of the air condensers just mentioned suggest very much fire tube boilers. According to one " school " of refinery practice, four towers are usually employed in

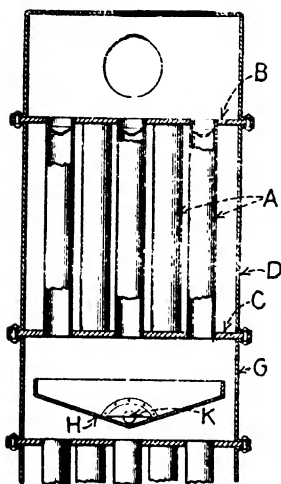connection with a single one thousand barrel crude still and each tower is made up of several, say three, superimposed and vertically connected (in series) condensing units. Figure 10 shows the details of one of these units[1] and Fig. 11 shows three of these units connected together vertically, thus forming a tower. Each unit (Fig. 10) consists of a series of tubes A secured in head plates B and C. A casing D surrounds the tubes and has openings E and F (Fig. 11) in order to allow currents of air to circulate around the tubes. Between the units D a flanged ring chamber G is interposed. This chamber contains a trough H which collects the condensate from the tubes and delivers it to water cooled condensers (Fig. 12) through a drain or spout K (Fig. 10).

Fig. 10. — Detail of tower section, vertical type.

With the arrangement of tubes and troughs shown in Figs. 10 and 11 the underside of each condensate receiving pan or trough acts as a baffle plate for the vapor passing upwardly through the tubes of the condensing unit just below the pan. Practice may vary as to whether the vapors enter at the top and leave through the bottom but it is considered better to have the vapors rise through the tower than vice versa. In Figs. 10 and 11 the tubes are shown as restricted by spiral baffles but this is not done in practice. In Fig. 12 is shown a diagrammatic assembly of a one thousand barrel crude still with four towers, each tower, excepting No. 4, made up of three units or " separations " as they sometimes are called. No. 4 tower consists as shown of a single set of long condensing tubes. This construction in the fourth or last tower of the series is intended to condense as large a proportion as possible of the vapors before they finally
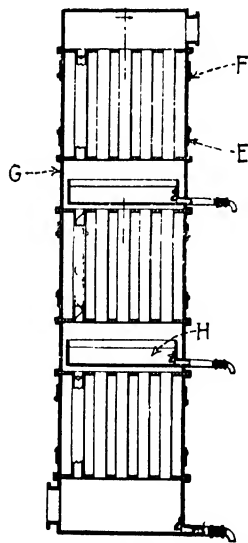

Fig. 11. — Diagram showing method of construction of vertical tower.

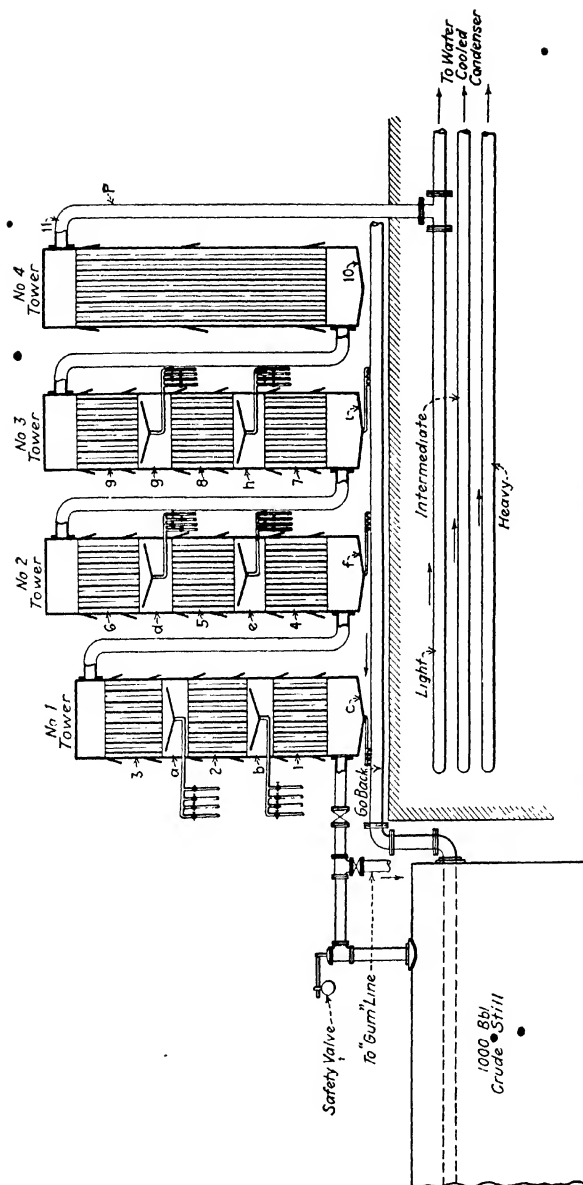[1] J. L. Gray, U. S. Patent 1,192,889, August 1, 1916.

Fig. 12. — Tower still for handling crude oil.

pass from the top of No. 4 tower into the water cooled condenser connected with it. In Fig. 12 each condensate receiving trough designated as *a*, *b*, *c*, *d*, etc., is connected to four headers or delivery pipes one of which is termed the " run back " or " go back," and condensate which is delivered into this header is returned or refluxed back into the still. The other three delivery pipes lead to separate water cooled condensers and they are termed " light," " intermediate " and " heavy " headers, respectively. Hence, condensate from each condensing unit falling into the trough located immediately beneath it may be directed by means of suitably arranged valves either back into the still for redistillation or through any of the headers just mentioned and by way of these headers into water cooled condensers and finally into the tail house. As shown in Fig. 12, the top of the fourth or last tower in the series is connected to the light header by means of a pipe *P*. This pipe is open at all times. The water cooled condensers are usually located beneath the " towers." The " towers " shown in Fig. 12 are either round or square in cross section, the casing surrounding the tubes on each condensing unit being provided with rather large openings which may be closed or opened by means of swinging shutters in order to admit currents of cold air or to insulate the tubes more or less as the case may be.

In operating on a paraffin or semi-paraffin crude oil it aids in securing a more perfect separation to operate the " go back," that is, to reflux the fractions to a considerable extent. This involves a certain amount of cracking and aids in the subsequent extraction of wax from the wax distillate. In coking an asphaltic crude oil, however, very little refluxing is permitted because an asphaltic oil is so sensitive that any considerable amount of refluxing would result in the production of too much coke. With paraffin and semi-paraffin crudes, the first four condensing units, that is all the units in tower No. 1 and one unit No. 4 in tower No. 2 are constantly refluxing or delivering into the " go back " during a large part of the distillation, particularly when heavy naphtha and burning oil are being produced, that is, until the paraffin or wax distillate begins to come over. Let us suppose that one thousand barrels of Illinois crude are being coked in a tower still. Up to the time the distillate is turned into the " gum line," [1] that is when the gravity of the stream which is going through the " heavy " header reaches about 11.7° Bé. gravity, the operation will have consumed say forty-five hours. During approximately the first half of this time the products which are running into the tail house have been light naphtha, heavy naphtha, and the burning oils, e.g., " water white," " standard white " and so on. Heavier " lubricating " oils have been distilling

[1] See Fig. 12.

but they have been refluxed back to the still owing to the fact that the first four condensing units are delivering into the " go back." During part of this time condensing units 5 to 10 inclusive (see Fig. 12) are delivering their condensates into the intermediate header. At first this intermediate stream delivers heavy naphtha and later on burning oil. During the whole of this time (the first half of the distillation period) and in fact during the whole of the distillation, vapors are passing from the top of No. 4 tower and delivering into the " light " header. At first this stream delivers light naphtha and then toward the end of the first half of the distillation period the light stream, constituted of vapors not condensed in No. 4 tower, is delivering burning oil (e.g., standard white). Now as the end of the first half of the distillation period approaches, more and more of the condensing units are arranged to deliver into the " go back " and a gradually decreasing number are permitted to deliver their contents to the tail house.

Hence the streams flowing into the tail house gradually diminish in volume until at the close of the first half of the distillation period the whole system of towers is refluxing. At this time there is only one stream running from the water cooled condensers, namely, the material not condensed in No. 4 tower and this stream now delivers burning oil. There remains in the still, owing to the refluxing just described, practically all the paraffin (lubricant and wax yielding) distillates, together with gas oil and including a small percentage of coke-yielding oils and wax tailings.

The method of bringing over the paraffin distillate consists in first adjusting the valves which control the flow of condensate from the first condensing unit, that is from the first trough or pan (the one nearest the delivery end of the vapor line from the still) so that the condensate flows into the tail house from this condensing unit through the " heavy " header instead of refluxing back to the still. Then gradually the other units are made to deliver their streams also to the tail house, mostly through the " intermediate " header. During the latter half of the total distillation period three streams are running to the tail house, a " heavy " stream from the first or first three or four condensing units, a " light " stream from the top of No. 4 tower and intermediate streams from the remainder of the condensing units. During this time both the intermediate and heavy streams consist of paraffin distillate. At the same time that paraffin distillate is being delivered by ten of the receiving troughs, " gas oil " is being delivered from the top of No. 4 tower, that is, it is constituted of vapors which are not condensed in any of the condensing units. It contains fractions identical in gravity with those of the burning oil distillate produced

during an earlier period of the distillation. The gas oil, however, comes over as mentioned at the same time that the paraffin distillate appears. The hydrocarbons composing this gas oil have obviously been exposed for a longer time and to a higher temperature than the hydrocarbons composing the burning oil crude fractions. Subsequently the gas oil distillate is worked up to obtain " gas naphtha," burning oil, and light and heavy gas oil. The tank gravity of the gas oil produced by the distillation of the crude is about 40° to 41° Bé. (All light naphtha produced by re-running gas oils is termed "gas naphtha." Gas naphtha is also the term more recently applied to the light naphtha obtained by re-running the " light distillate " from pressure stills.)

The residue from working up gas oil produced in the crude distillation, to obtain naphtha and burning oil, constitutes part of the charging stock put into tube stills or shell stills for cracking to make gas naphtha. This will be considered later. The gas oil referred to above is only one of the several grades of oils classed in the refinery as " gas oil." Gas oils are very extensively used for cracking purposes. They are also used to carburet water-gas from which function their name is derived and in this treatment they are decomposed to a profound extent yielding ethane, propane, ethylene, propylene, benzol, toluol, methane, hydrogen and other hydrocarbons.

The above description has been limited to the complete distillation of a typical semi-paraffin crude oil in a single or batch " tower " still. As a matter of fact these tower stills are built in series or batteries and are connected in such a way that they may be operated continuously, that is crude oil may be pumped into the first still in the battery and residuum pumped out of the last still. Any individual still in the battery may be cut out of this continuous system at will and operated as a batch still as occasion demands. For example gas oil is very commonly re-run through these tower stills continuously and distilled by direct fire. This separates the material into light or "overhead" stock consisting of gas naphtha, burning oil and light gas oil, and produces a residue of heavy gas oil. It is also quite common to operate the tower stills continuously to produce " reduced crude." Suppose a battery of five tower stills, for example, is used to make reduced crude, for the purpose of skimming off naphtha, burning oil and gas oil and obtaining a residue consisting largely of lubricant and wax yielding fractions. The " go back " on the first four stills might advantageously, in this case, be operated in order to effect a better separation of the naphthas and burning oils but the last still in the series should not reflux at all under these conditions, in order to eliminate everything except the lubricant and wax yielding fractions. In such
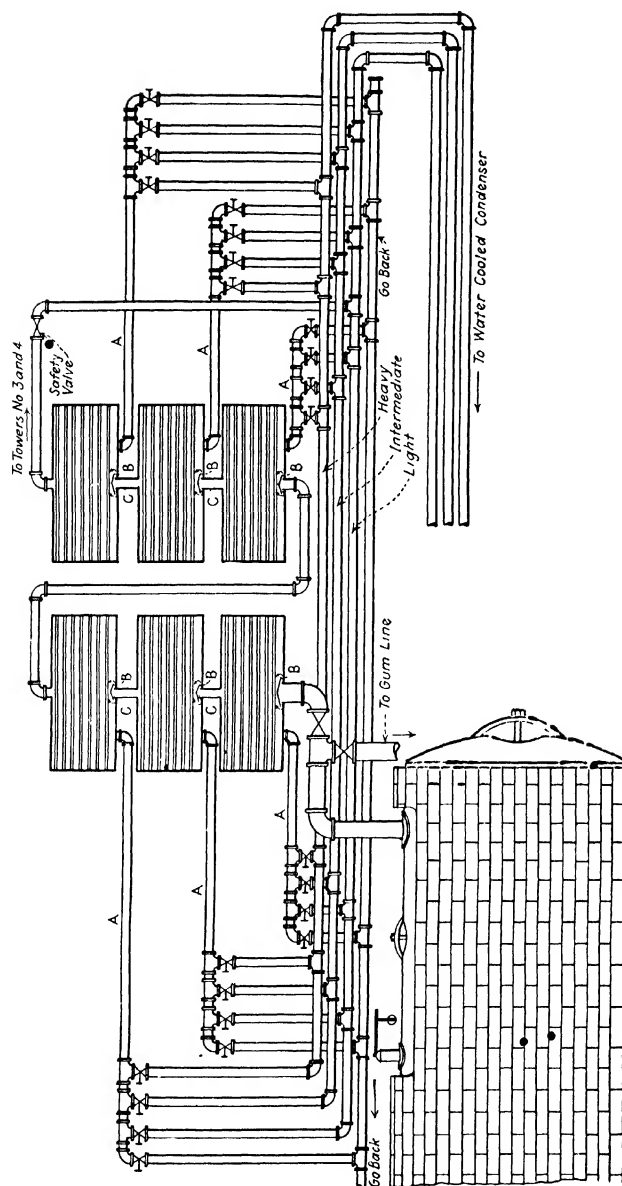
Fig. 13. — Tower still with horizontal towers.

a battery of five stills for producing reduced crude, the first group
would produce continuously light and heavy naphtha, the next group
various grades of burning oil and the last still would produce heavy
burning oil and gas oil. (The method of connecting up stills to operate
continuously will be described and illustrated in connection with the
steam refining of gas naphtha.)

Figure 13 shows a form of an aerial condenser and tower which is
considered by some to have advantages over the vertical square or
cylindrical tower. Here again the analogy with the steam boiler is
apparent since the condensing unit is in effect a tube boiler. Each tower
consists of several superimposed horizontal cylindrical shells traversed
longitudinally by a number of tubes. The oil vapors pass through the
shell and are subjected to cooling and condensing action on the surfaces
of the tubes. The condensing shells or units are connected together by
passageways as shown at *C* in Fig. 13 and condensate which collects
on the bottom of the shell may be prevented from flowing back into
the next lower shell by means of a lip as shown at *B*. As in the case of
the older square towers, each condensing unit or shell is connected
through drain pipes [1] as shown at *A* with each of four headers, the
" go back," " heavy," " intermediate " and " light " headers. It is
easy to see one advantage of this form of tower over the older types of
square tower, inasmuch as all parts of these cylindrical condensing
units are easily accessible and may be easily repaired. The top of
the last condensing unit in the series is as usual connected with the
light header.

As an example of the yields of the various fractions from a crude distillation of a
semi-paraffin oil the yields from the distillation of an Illinois crude described some-
what in detail above are given:

Light Naphtha . . . . 61½°–65° Bé.	12 per cent
Heavy Naphtha . . . . 53°–54° Bé.	13 " "
Burning Oil . . .. 42°–47° Bé.	15 " "
Gas Oil ... . 40°–41° Bé.	21 " "
Paraffin Distillate .. . . 29½°–30° Bé.	28 " "
Slop Paraffin Distillate . . . . 20° Bé.	6 " "
Wax Tailings and Coke	3 " "
Loss.....	2 " "

All the crude fractions with the exception of the paraffin distillate,
wax tailings and coke are sources of light naphtha. Heavy naphtha,
for example, on re-running in steam stills yields light naphtha and a
residue which may be used to augment the burning oil fraction. Treated
burning oil, similarly, when steam refined to raise its flash and fire

[1] These drain pipes are often termed " run-down lines."

test, yields some heavy naphtha and a residue of " fire test burning oil."
It has already been mentioned that gas oil produced by the distilla-
tion of the crude, when re-run, yields gas naphtha as one of the products.
Hence, in order partially to reproduce the fractions of petroleum as
they supposedly exist in the crude oil it is necessary after the crude
distillation constantly to rework these fractions, that is redistill, in
order to extract from them those hydrocarbons which belong in the
next lower and next higher boiling fractions. This constant reworking
requires a large amount of heat, in addition to the heat required in the
distillation of the crude, and so a considerable part of the ingenuity
and experience possessed by oil refiners and engineers is directed to
the conservation of heat. Heat exchangers or economizers are there-
fore in extensive application in refineries and it is one of the advan-
·tages of the continuous methods of distillation that they permit the
convenient use of heat exchanging devices. This is true in the case
of all continuous distillations which take place whether it is a ques-
tion of reducing crude oil, re-running heavy naphtha, raising the
fire test of burning oils or re-running gas oil. The best practice ad-
vises wherever possible conducting these operations in a battery of
continuous stills and utilizing heat exchangers wherever possible. A
typical example of the application of heat exchangers to a battery of
steam stills as well as the method of connecting stills so that they operate
continuously (whether steam or fire stills) will be taken up in connec-
tion with the re-running of blended gas naphtha to produce commercial
motor fuel

Following the separation of the crude oil into the fractions which
are in demand by the oil trade, chemical treatment must be resorted
to in order to put the oils in an acceptable and utilizable condition.
For well known reasons sulphur compounds and a considerable portion
of the unsaturated hydrocarbons in the crude fractions must be removed.
The desulphurization of naphtha and burning oil is sometimes more
troublesome than the ordinary treatment for removing unsaturated hy-
drocarbons. The latter calls for treatment with sulphuric acid of suit-
able strength, usually at the ordinary or even lower temperatures,
while desulphurization in the case of the refractory sulphur compounds
which occur in very " sour " oils require chemical treatment with a
special desulphurizing agent, usually a form of copper oxide known in
the refineries as " copper compound." This statement has particular
reference to the sour oils which formerly were obtained in large quantities
near Lima, Ohio. The output of these sour crudes has greatly de-
creased in recent years, with the result that the copper oxide treatment
is not now of such importance as formerly. The general practice for

removing sulphur at the present time consists in treatment with sulphuric acid followed by sodium plumbite, and it is believed by some
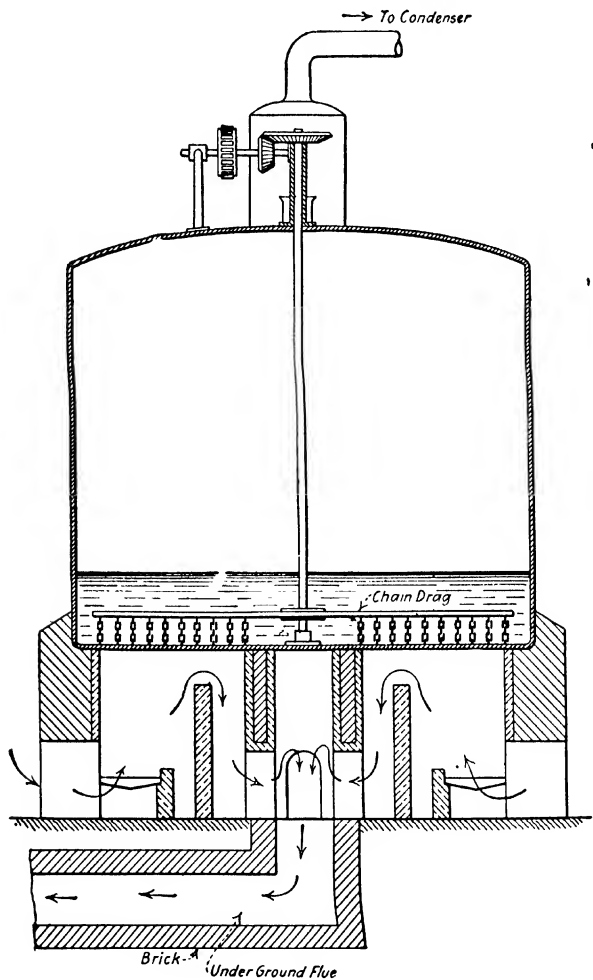

Fig. 14. — Cheese box still used for desulphurizing "sour" oils. The latter were distilled in the presence of a form of copper oxide familiarly known as "copper compound." The chain drag served to keep the desulphurizing agent in suspension in the oil.

that of these two reagents, the sulphuric acid exerts the more pronounced action. The sulphur compounds in oils have been the subject of considerable investigation and the form in which these sulphur

compounds occur in oils from various localities has been at least partly determined in a number of cases. Oils from which the sulphur can be removed by means of sulphuric acid and sodium plumbite are sometimes called semi-sour oils, whereas those, the sulphur compounds of which are not largely removed in this way are characterized as "sour." Sodium plumbite is referred to in the refineries as the "doctor" and it is prepared by "saturating" strong caustic soda solution with litharge (lead monoxide).

When treating a distillate with sodium plumbite, pretreatment with sulphuric acid is advisable but not always necessary. The "doctor" treatment consists in agitating the distillate with sodium plumbite. After settling and drawing off the "doctor" solution, flowers of sulphur are added and agitation resumed. The sulphur decomposes excess plumbite with the formation of lead sulphide which settles out. A final water wash completes the "doctor" treatment.

The cracking of gas oils to produce gas naphtha is conducted to such a large extent at the present time that gasoline produced from this source constitutes an important part of naphtha and the motor fuel of commerce. Although the best cracking processes produce a gas naphtha with a minimum percentage of unsaturated hydrocarbons, nevertheless this synthetic gasoline, as it may be called, always possesses a higher unsaturated value than that which is produced by the straight distillation of the paraffin and semi-paraffin crudes. It is desirable therefore in utilizing gas naphtha produced by cracking processes to blend it with so much of the straight distilled product that the resultant material will, after treatment with acid and steam distillation, yield a product free from objectionable features when used for motor fuel and other purposes. This blending is carried out in such a way that the gravity of the blend will (after treatment with acid, say two and three-quarters to three and a quarter carboys of the acid [1] to one hundred barrels of naphtha) be about 58° to 59° Bé., $58\frac{1}{2}$° Bé. being a typical value. The treatment with acid is possibly most economically carried out on a large scale in continuous treaters instead of in the older type of agitator. There may be discussion as to just how much economy is effected in this way but at any rate continuous treating occupies a place in the refining of light naphtha. It is not applied to heavy naphtha or burning oil. The term continuous treating may be regarded by some in part at least as a misnomer. It might be supposed from the word continuous that the treatment consisted in uninterruptedly washing a stream of naphtha going in one

[1] Sulphuric acid of 66° Bé. commonly is used, but somewhat weaker acid is now recommended in order to reduce refining losses.
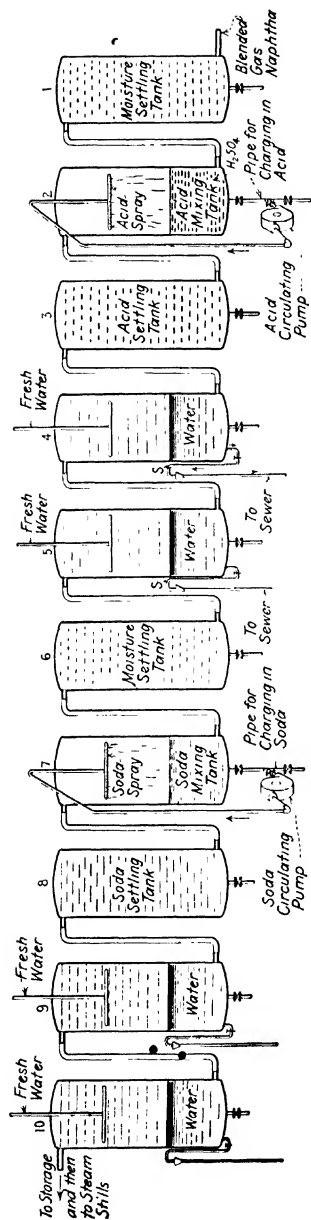
Fig. 15. — Diagram outlining the continuous method for treating naphtha.

direction by a stream of acid coming in a counter current direction. This however is not strictly the case. The treatment consists, so far as the acid is concerned, in pumping the naphtha through an upright cylindrical shell which is partly filled with sulphuric acid. The naphtha enters at the bottom of the shell, passes up through the acid, collects on top of the acid and fills the shell and then flows into the next tank. As shown in the diagrammatic sketch (Fig. 15), while the naphtha is passing through the acid mixing tank or shell a circulating pump withdraws acid from the bottom of the shell and sprays it into the upper part of the shell from whence it rains in streams through the ascending body of naphtha. A given quantity of acid is first charged into the acid mixing shell and when a quantity of naphtha has been pumped through that shell in the proportion of one hundred barrels of naphtha to from two and three-quarters to three and one-quarter carboys of 66° Bé. sulphuric acid, the treatment, that is the pumping of the naphtha and the circulating of the acid, is stopped, the acid sludge drawn off and a quantity of fresh acid added before treatment is resumed. In this respect therefore the process is discontinuous. The pumping is carried on slowly enough so as to insure that the naphtha will be thoroughly acted upon by the acid. The construction of the acid mixing shell is extremely simple. Nevertheless it, together with the other parts of the continuous treaters, has been evolved only after many

years of experimenting. Following the acid mixing tank the naphtha passes through an empty shell where particles of acid carried over from the mixer have an opportunity to settle. Two water washing tanks, each like the other, then follow in the series. They contain water to about one-third of their depth which is kept in a fresh condition by a constant supply of fresh water through a spray in the upper part of the shell, while the acid washings are constantly drained off through a pipe at the bottom of the shell which delivers into a sight feed as shown at S (Fig. 15). A moisture settling tank then follows and next the soda mixing tank (which is operated in all respects like the acid mixing tank), next a soda settling tank and finally two water washing tanks or shells follow. The naphtha after passing through the last tank in this series of continuous treaters passes to storage tanks before being submitted to a steam distillation.

As previously mentioned gas naphtha resulting from the cracking of gas oil in pressure stills is blended with straight distilled naphtha in such proportions that the gravity of the mixture after chemical treatment, as described above, is in the neighborhood of 58° to 60° Bé. This is the material which yields commercial gasoline after treatment in steam stills. Steam distillation is most economically carried out on a large scale by means of continuous steam stills which may be operated in a battery of five as shown in Fig. 16. The stills in this battery are connected together at one end by a header (P, Fig. 16). From this header branch pipes enter each still (as shown at Q, Fig. 16) in such a way that oil flows from the end of one still through the header P and into the farther end of the next succeeding still in the battery. That is to say of the two branch pipes which enter each still (except the first still in the series) one of these branch pipes (as shown by K_1, K_2, K_3 and K_4, Fig. 16) extends the full length of the still whereas the other merely enters a short distance inside the still. The longer of the two pipes is the one which conducts the oil into the still and the shorter is the one through which the oil flows out of the still. These branch pipes enter at the same level on all the stills. Moreover each still is provided with an oil cooled reflux condenser which also acts as a heat interchanger, through which vapors pass before entering the water cooled condenser. The first still in the battery has, in addition, a large dephlegmating tower (C, Fig. 16). The distillate from the first still therefore passes first through this dephlegmating tower C, which is packed with bits of brick, stone or other ceramic ware, then through the oil cooled condenser H_1 and finally through a water cooled condenser. Treated and blended gas naphtha comes from storage tanks, is pumped through the heat exchangers or oil cooled reflux condensers
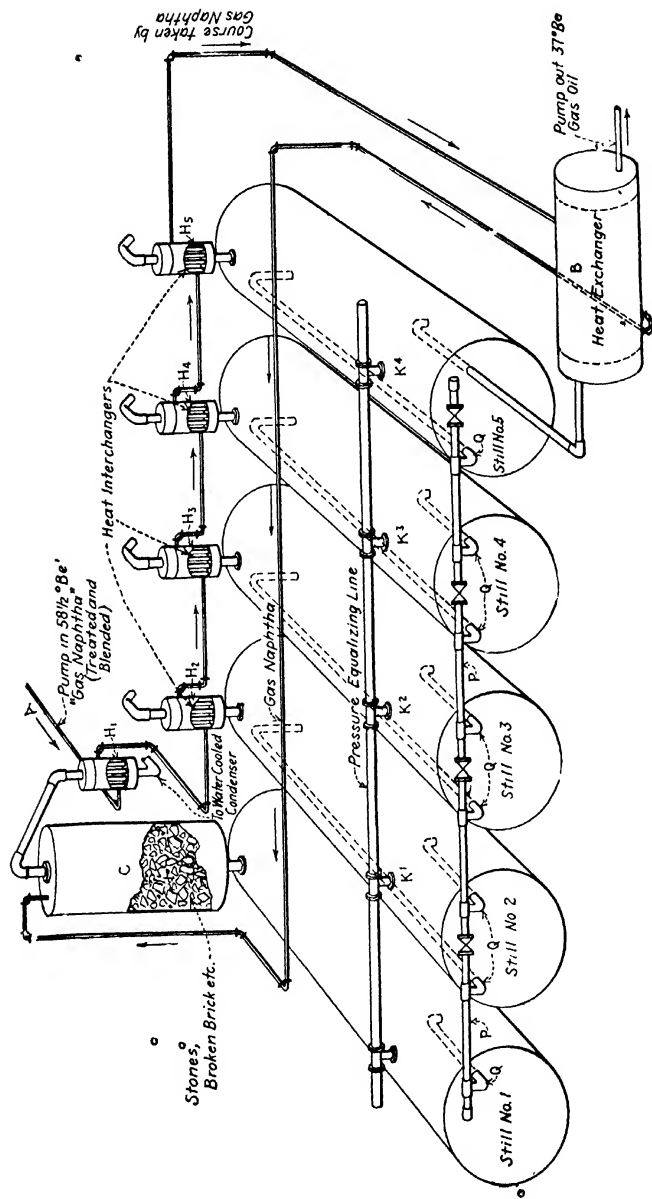
Fig. 16. — Group of steam stills for refining naphtha connected so as to operate continuously.

H_1, H_2, H_3, H_4, H_5, then through a large heat exchanger B (where it is heated by the residue of gas oil which is being continuously pumped from still No. 5), and is then pumped back in the direction shown by the arrows to still No. 1 and enters this still at the top of the dephlegmating tower C. Before entering the still itself the naphtha is further heated by the hot vapors and condensates in the tower C. Providing the gravity of the gas naphtha which is being pumped through the
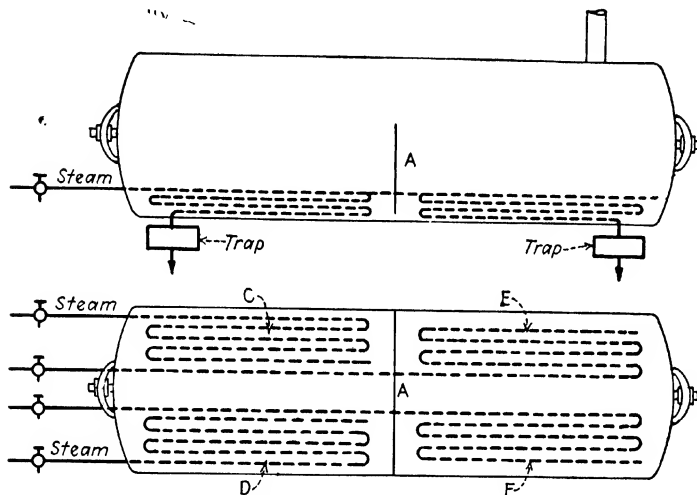

Fig. 17. — Detail of steam still showing heating arrangements.

various heat exchangers is about $58\frac{1}{2}°$ Bé. the still No. 1 will continuously yield light naphtha of gravity 69 to 70. Still No. 2 will yield naphtha of gravity say 59.1, still No. 3, naphtha of a gravity of about 55.1, still No. 4, naphtha of a gravity of approximately 52.5 and still No. 5, naphtha of a gravity of about 49.8. The residue which is continuously pumped from still No. 5 will in this case be approximately a 37° Bé. gas oil. By the arrangement shown in Fig. 16 it is seen that a considerable amount of heat economy is effected. Besides the header which connects the stills at the ends of the same for a continuous flow from one still to the other, there is also a header which extends along the top of the stills and which equalizes the pressure in each still and makes for more uniform distillation; that is, any undue pressure in one still is immediately minimized by distribution through the other stills in the battery. A somewhat more detailed diagrammatic view of a single steam still is shown in Fig. 17. The upper view shows an eleva-

tion and the lower view a plan. As shown in Fig. 17, there is a vertical partition A situated at about the middle section of the still which has an opening at the bottom to permit free transfer of liquid from the one portion of the still to the other. Steam coils C, D, E and F lie on either side of this partition and are controlled by valves situated at the one end of the still as shown (Fig. 17). The portion of the still nearest to where the steam enters the coils is naturally somewhat hotter than the parts of the still farthest from where the steam enters owing to condensation. This gives rise to a certain amount of convection inside the still and it has been found that this convection is aided by the presence of the partition A; hence in this way a more uniform vaporization takes place. Older types of steam stills whether continuous or not are provided with some such means as this to enable the maintenance of uniform conditions of heat inside the still. In each of the coils, C, D, E and F shown in Fig. 17 there are about five hundred feet of two-inch pipe. Steam traps on the bottom of the still collect the condensate from the coils.[1]

Distillation by Means of Perforated Steam Coils. — Present practice for the production of finished gasoline from naptha by steam distillation favors simply treatment by blowing steam through the naptha and condensing the distillate. This does not require the use of the heating coils shown above. In other words, according to present practice, the treated naptha is charged into a still provided with perforated steam coils and steam is blown through the naptha to distill gasoline.

Cracking Heavy Oils in Pressure Stills. — Of the immense number of processes which have been proposed and tried for the purpose of decomposing heavy by-product oils into naphtha, those methods which are based upon the distillation and condensation under pressure are

[1] **Navy Specifications for Gasoline**

There are two Navy specifications, the old and new, in accordance with which most of the larger refiners have made and are still making their products conform, approximately at least. The new Navy specification is more liberal than the old one and consequently there is a tendency toward the use of the former. The War Department has also adopted the new specification as a standard for its requirements for motor gasoline.

Old Navy Specification	*New Navy Specifications*
Initial Boiling Point 140° F. (60° C.)	Initial Boiling Point, 140° F. (60° C.)
20% off below 221° F. (105° C.)	20% off at 221 F. (105° C.)
45% off below 275° F. (135° C.)	50% off at 284° F (140° C.)
90% off below 356° F. (180° C.)	90% off at 374° F. (190° C.)
95% off below 428° F. (220° C.)	Dry Point 437° F. (225° C.)
95% of the liquid recovered from the distillation of 100 cubic centimeters	95% must be recovered.

in most extended use today. These methods also include the combination of oil circulating tubes in series with the still itself. In fact the combination of the still with circulating tubes combined with condensation of the distillates under pressure is the method which is looked upon with most favor at the present time. The Burton process is a typical example of distillation and condensation under pressure. When these processes were first put into practice, shell stil's were employed, which are described in the chapter on the Burton Process and consist essentially of a simple shell connected with an inclined vapor line and then with the water cooled condenser. One of the difficulties with this type of still was the accumulation of carbon deposits upon the bottom of the shell which led to not infrequent periods when the apparatus had to be put out of service in order to be cleaned or repaired. Accidents were not uncommon and are not uncommon today owing to this accumulation of carbon and consequent burning out of the bottom of the shell. Of late years these simple shell stills have been superseded considerably by what are known as tube stills which are very similar in appearance to an ordinary water tube boiler. The advantage lies partly in the fact that it is the tubes which receive the most intense heat and owing to convection currents, oil is constantly circulating through these tubes. This circulation prevents in a large measure the deposition of coke or carbon and this is true especially of the bottom of the drum or superimposed shell. With the old type of shell stills it is necessary to send men into the still at the close of a run or series of runs, in order to clean out the carbon, and in some plants it has been found difficult to obtain the labor necessary. The employment of the tube still, which was developed by **Clark,** obviates this labor difficulty to a considerable extent, inasmuch as the circulation of hot oil through the tubes exerts a scouring action and tends to prevent carbon deposit. The use of this type of still probably involves a greater fire risk than stills of more simple construction. When overheated or worn too thin, the bottom of a plain pressure still will bulge and thus give warning of impending trouble. A tubular heating auxiliary, however, cannot be so readily inspected. When a tube burns out the defect is not observed until the oil pours into the fire and with a pressure of 75 pounds per square inch, or higher, thousands of gallons of superheated oil can discharge into the fire box in a very brief space of time. Burning oil running out of the fire box is likely to set fire to overhead construction and cause considerable damage. Hence great pains are taken to arrange the overhead construction in such a way that a tube blow-out will cause a minimum of damage. The improvement in refinery practice with respect to the operation of pressure stills has
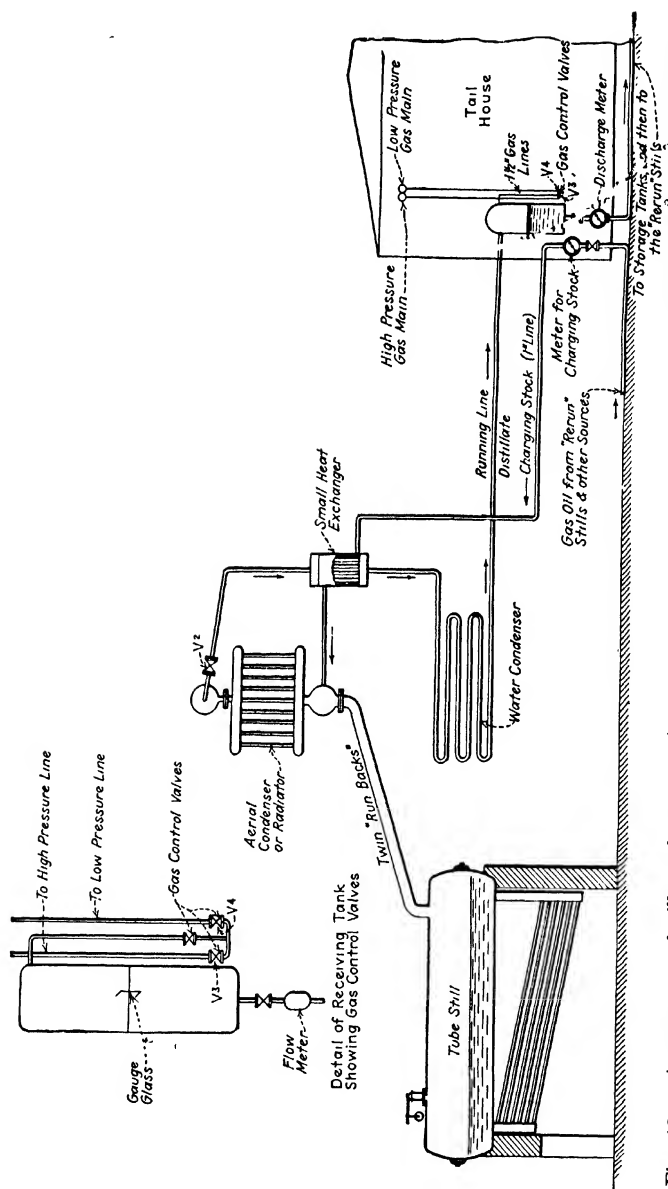
Fig. 18. — Arrangement of still, condensers, receiver, meters and connections incident to the operation of a tube pressure still.

seen a very considerable amount of growth in the past half dozen years. The reader is referred to the chapter on the Burton Process and the chapter on Distillation Under Pressure for a more detailed account of this evolution. In the present chapter it is attempted merely to give what is believed to be a resumé of typical present day practice. The description is therefore confined to the method of assembly and operation of a battery of so-called " tube stills " and accessory apparatus.

Referring to Figs. 18 and 19, each still in the battery is provided with an inclined vapor line or lines which consist of two large pipes located
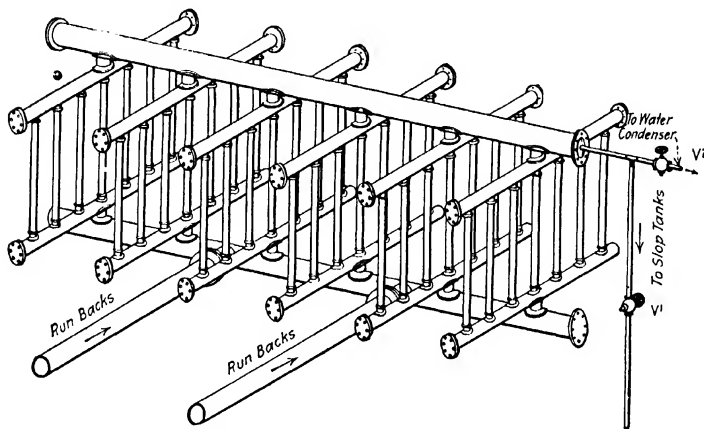

Fig. 19. — Air condenser or "radiator" with inclined vapor pipes ("run backs").

in the same inclined plane and called " run backs." As shown to better advantage in Fig. 19 these run backs are connected to the lower header of an air reflux-condenser called " radiator." This " radiator " consists of two large headers located in the same vertical plane and connected together by a series of heat radiating tubes, each series of tubes being in the form of a grid. The method of cracking gas oils by distillation under pressure is not a rapid process nor are the gas oils by any means quantitatively decomposed into hydrocarbons within the range of gasoline. A considerable amount of cracking takes place which goes only as far as to produce hydrocarbons of the burning oil group. It is partly the function of the aerial condenser to condense and return to the still those fractions which it is desired to avoid being carried over into the tail house. There is also a certain amount of uncracked heavy oil which tends to pass along with the lighter vapors and whose separation from these lighter vapors is aided by the aerial condenser. From the end of the topmost header on this condenser a line in some cases

provided with a valve, V_2, leads to the water condenser. This valve, V_2, is sometimes used in building up pressure in the still although more recent practice effects the same object by valves located in the tail house, as will be described later. Another valve V_1 in a branch pipe as shown in Fig. 19 is used through which to distill off water when
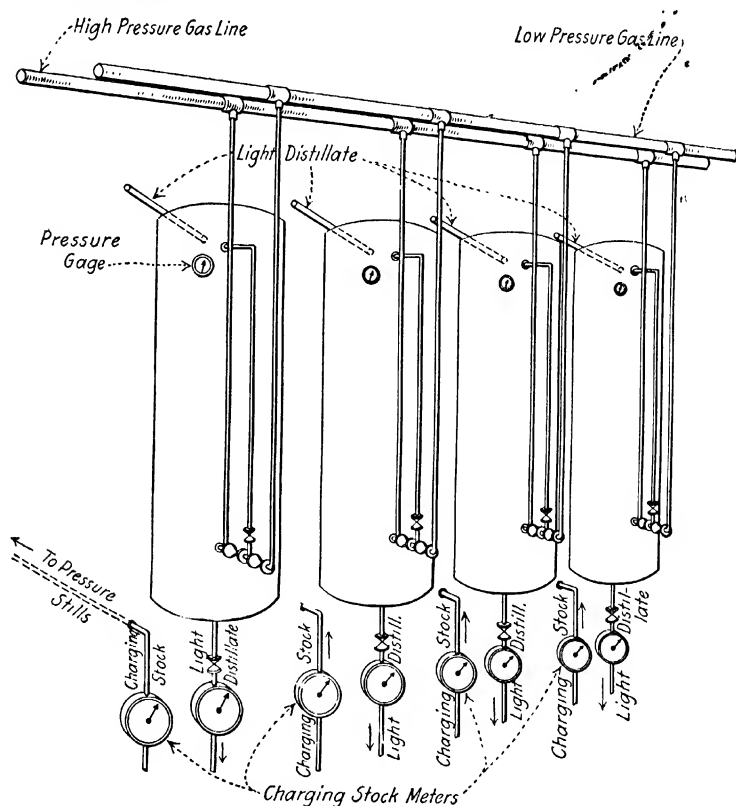

Fig. 20. — Portion of interior of tail house, showing receiving drums and accessories.

the still is first fired up. Between the aerial condenser and water cooled condenser there is interposed a small heat exchanger as shown in Fig. 18 through which it is often customary to pump the charging stock during operation. This heat exchanger is only a small affair,[1]

[1] Another method, and one which is in use at the present time, does not employ the air condenser or radiator in the manner shown but uses a heat exchanger to cool and dephlegmate the vapors directly as they come from the still. This latter method was developed by **Hopkins**. (See also A. S. Hopkins, in the chapter on the Burton Process.)

say about four feet long. The vapors pass through the *tubes* in this exchanger whereas the charging stock passes through the *shell* in a direction counter-current to that of the vapors. From the aerial condenser the vapors pass through the heat exchanger and water cooled condenser and a running line (without passing through any valves) to the receiving drum in the tail house, in which the condensed vapors settle, partially filling the receiving drum to a point which is indicated by a gage glass. The uncondensed vapors collect under pressure in the upper part of the drum. The condensed hydrocarbons are now called "light distillate." From the upper part of the receiving drum a small gas line drops down to a "tee" within easy access of the still man. From this tee two small, say one and one-half inch, gas branch lines lead up to two corresponding gas pressure mains. Each of the branch pipes mentioned is provided near the tee with a valve (see V_3 and V_4, Fig. 18). From the bottom of the receiving drum a discharge pipe leads through a valve into a discharge meter. From the meter the "light distillate" passes out of the tail house to storage tanks and then to the "re-run" stills. Located near the discharge meter is also the meter which registers the flow of charging stock for the tube still, that is to say the charging stock before entering the still passes through the tail house and is gaged by the still man. It follows that there is concentrated in this way within a small sphere of action practically all the elements of control which are vital to the safe operation of the still. Each still in the battery is similarly provided with a receiving drum, gas control valves and meters for light distillate and charging stock. A portion of the interior of a tail house showing diagrammatically the position of the receiving drums and their accessories is shown in Fig. 20.

To aid in a more uniform maintenance of pressure in all the stills, the receiving drums as shown are connected together through the gas pressure control valves with the overhead high pressure mains. Thus any excess of pressure in one still may easily be dissipated by distributing that pressure among all the other operating stills in the battery. The tube stills may be run continuously. It is quite often the case that there is a certain amount of charging stock more or less continuously pumped into the still during the progress of the distillation. For example about 250 to 260 barrels of charging stock may be pumped in before firing up, and while say about four barrels per hour are being run off, two and one-half barrels per hour are pumped in through the heat exchanger. The point where this fresh charging stock enters is, as shown in Fig. 18, in the lower part of the aerial condenser. In some cases it is considered very good practice to run off about sixty per cent of the total charge regardless of the
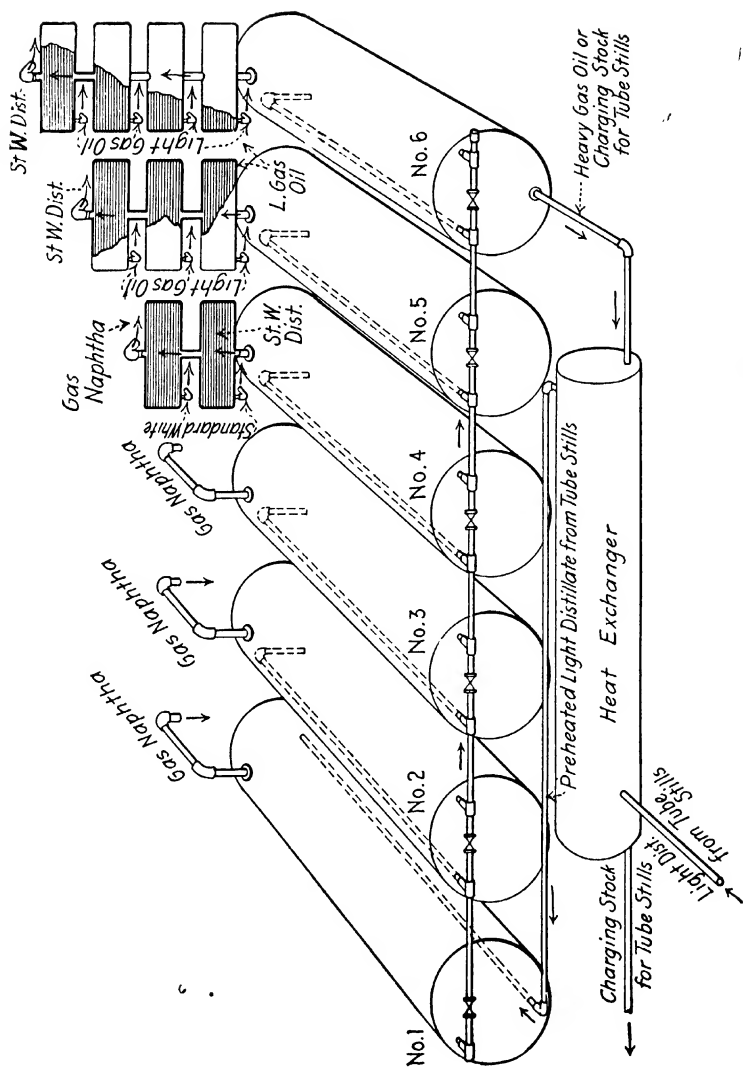
Fig. 21. — Battery of continuous fire stills.

gravity of the " stream." Usually however the gravity of the stream when operating on paraffin and semi-paraffin gas oils will commence at about 65° Bé., and end at about 46° Bé., and the tank gravity of this material will be 48° to 50° Bé. The residue in the still is called " pressure tar " and has a gravity in the case just mentioned of about 25° Bé. It is often mixed with other oils and sold as fuel oil.[1] A typical charging stock is a gas oil which has a gravity of say 34° to 38° Bé. and of which about thirty per cent will come off below 550° F. (288°C.).

Referring again to Figs. 18 and 20 each receiving drum is provided with a pressure gage and this is maintained in the neighborhood of seventy-five pounds during the distillation. Excess pressure is relieved through V_3 into the high pressure gas main. At the end of the operation, however, valve V_4 leading into the low pressure gas main is opened while valve V_3 leading to the high pressure gas main is closed. The pressure in the still is relieved into the low pressure gas main down to about forty pounds when valve V_4 is again closed and the remaining pressure in the still is utilized for blowing the residue or pressure tar out of the still. The so-called " light distillate" having a tank gravity of about 49° Bé. is now re-run in fire stills to distill off gas naphtha. This may be done in a single fire still or on a larger scale in a battery of continuous fire stills. Such a battery of continuous stills is shown in Fig. 21. As shown here the light distillate from the tube stills is continuously pumped into still No. 1, first passing through a large heat exchanger and being preheated in this manner by the hot residue of heavy gas oil which is continuously pumped from still No. 6. This residue of heavy gas oil is then passed to a tank where it may be mixed with heavy gas oil from other sources and the whole, called charging stock, then utilized for cracking in the tube stills. As shown in Fig. 21, the first three stills are not provided with towers and when this battery of stills is being run on light distillate, these first three stills will continuously yield gas naphtha suitable for mixing with straight distilled light naphtha to make " treating stock." The last three stills in the battery are however provided with separating towers (see also Fig. 22). The condensing units on these towers are provided in the usual way with a drain which leads either to a "go-back" or any one of three independent condenser coils. If, in the operation of re-running the light distillate, it is desired to separate the residue as closely as possible, then the go-backs on the stills provided with towers will be operated to a considerable

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[1] The pressure still " tar," as it is called, from a pressure still of the Burton type is regarded as a high grade fuel. It has a calorific value ranging in the neighborhood of 19,600 B.t.u. Although containing carbon it is quite a fluid oil and burns very satisfactorily.

These Towers
separate heavy
Naphtha, burning
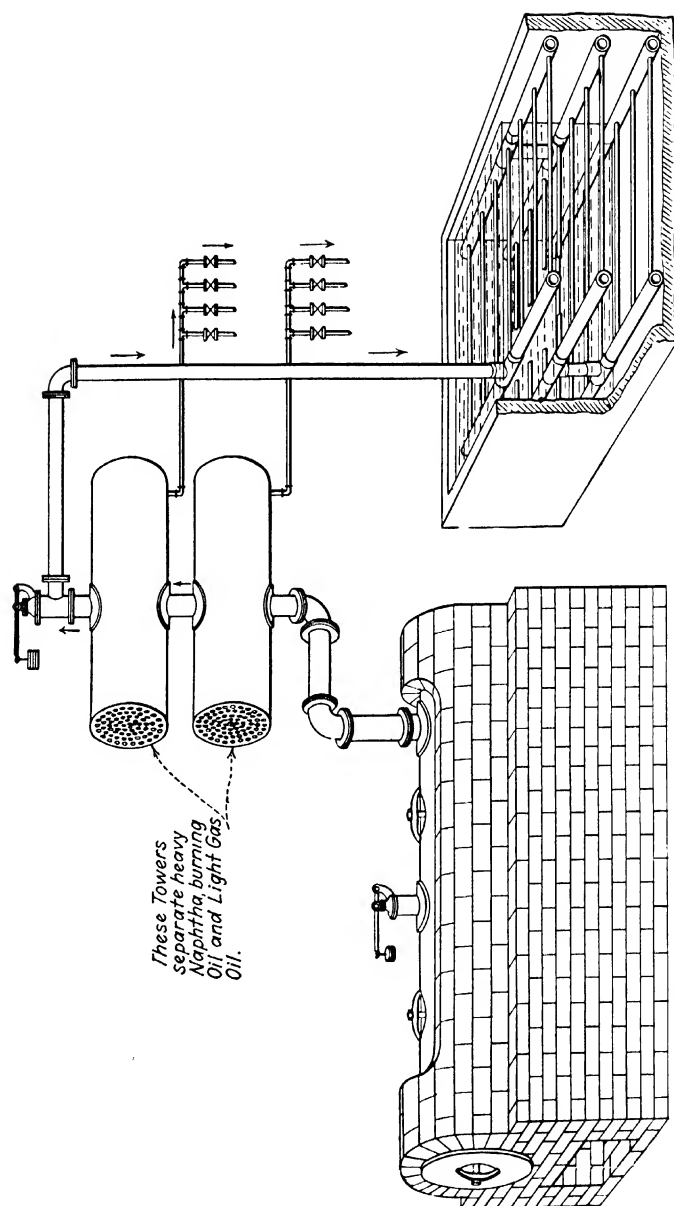Oil and Light Gas,
Oil.

Fig. 22. — Fire still provided with horizontal towers.

extent. But instead of each go-back delivering into its respective still, all the go-backs, for purposes of more complete separation,. would in this case lead into still No. 3. The yield of " gas-naphtha " where the charging stock is paraffin or semi-paraffin gas oil of say 36° Bé. gravity and of which twenty-five to thirty per cent comes off below 550° F. (288° C.) would be approximately twenty per cent of the original charging stock placed in the tube still. This then is a measure of the efficiency of that method of cracking heavy oils which is in largest use at the present time. It is contended that the amount of gas formed in the tube stills per gallon of gas naphtha produced is lower than in any other process for cracking oils to make naphtha.

Referring again to Fig. 21 where the use of the go-backs is mentioned, attention is called to the fact that in this re-running process the light distillate from the tube stills yields, beside gas naphtha, burning oils and light gas oil as distillates. In Fig. 21, connected with the illustration of each condensing unit there is attached a notation which indicates the nature of the distillates which may be expected to be yielded at various points in the towers. Figure 22 shows somewhat more in detail, in diagrammatic form, the connections on the re-run stills and towers. It will be understood that the towers may be of the older vertical type instead of the horizontal type shown.

II. The Production of Naphtha by the Distillation of Heavy Asphaltic Crudes

Coking Stills for Mexican and Other Asphaltic Oils. — In the treatment of such crudes, water offers even more difficulty than it does in the case of the paraffin crudes. The nature of the asphaltic petroleums is such that the water which they very often contain clings to them with great tenacity and offers considerable difficulty in case it is attempted to expel the water in ordinary stills. As is well known, attempts to treat a wet asphaltic crude in an ordinary still results in frothing, bumping and the effect technically known as " puking." This difficulty is overcome by submitting the oil to a preliminary distillation in a tube or "pipe " still.

Such a still is shown diagrammatically in Fig. 23. As shown, this still consists of a continuous coil of six-inch pipe made up in twelve-foot horizontal lengths connected together at their ends by means of return bends. The discharge end of the coil is connected with a superimposed receiving or separating drum which is so arranged in the furnace setting as to be heated by the hot gases of combustion. A vapor line leads from the top of the separating drum to a water cooled condenser and

the level of hot oil discharged into the receiving drum is maintained nearly constant by means of a discharge or drain line which conducts the dehydrated oil into the shell of a heat-exchanger through which the wet crude passes in counter-current direction on its way to the
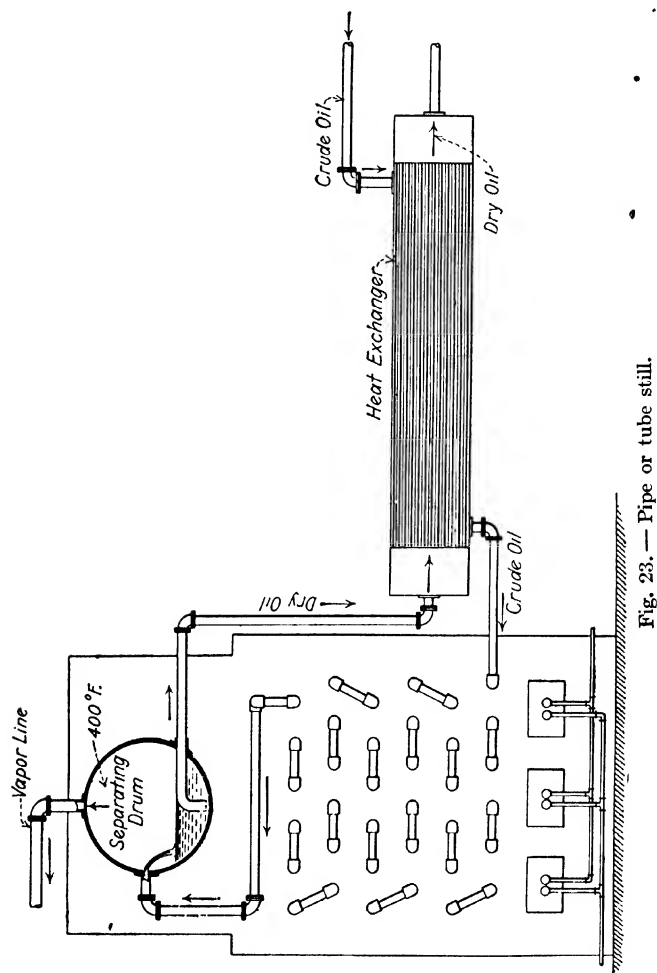

Fig. 23. — Pipe or tube still.

dehydrating tubes. Although the primary object of the still is dehydration, the apparatus functions also, partially at least, as a topping still inasmuch as a certain amount of naphtha is distilled off with the water. The fires are so regulated and the oils are pumped through the tubes at

such a rate that the temperature of the vapors as they leave the separating drum is in the neighborhood of 400° F.[1] One of the objects of keeping the separating drum at about this temperature is to prevent condensation of water in it. After the heavy crude has gone through this dehydrating or " topping " action it is in a condition for further treatment in stills. This treatment will depend entirely upon whether the refinery practice is concerned with the production of lubricating oils or whether the crude is to be reduced to make asphalt. In making lubricating oils the dehydrated crude is distilled to coke. This will result in the production of light and heavy naphtha, burning oil, gas oil, light and heavy lubricating stock, gas and coke. In the case of
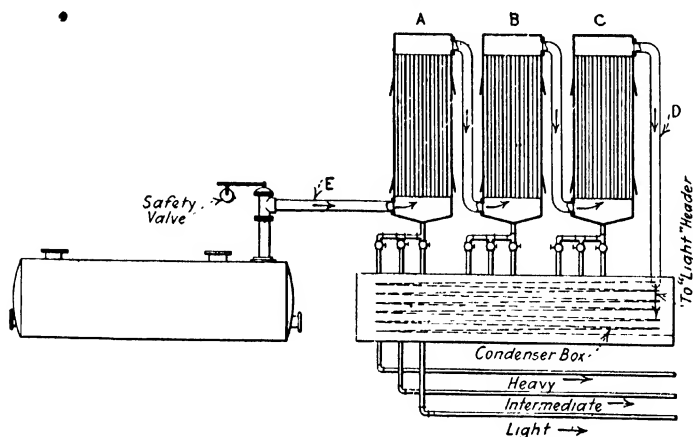

Fig. 24. — Tower still for coking asphaltic crude oil.

certain asphaltic oils containing paraffin a wax distillate will also be obtained simultaneously with the lubricating stock. The amount of light and heavy naphtha obtained is not always dependent upon the percentage which is naturally contained in the crude. The asphaltic crudes are of such an unstable and unsaturated nature that it is not difficult to promote cracking. However many of the Mexican crudes, for example, contain a considerable amount of naphtha, as such. The coking takes place in ordinary coking stills which are provided with air condensers or towers. As shown in Fig. 24, these towers are of the usual vertical tubular type but do not contain as many separate units as in the case of towers connected with stills which are used to coke paraffin and semi-paraffin crudes. Three towers are often sufficient and, as shown in Fig. 24, are built up of a single set of long tubes. The bottom of each tower is arranged to deliver into any one of three separate
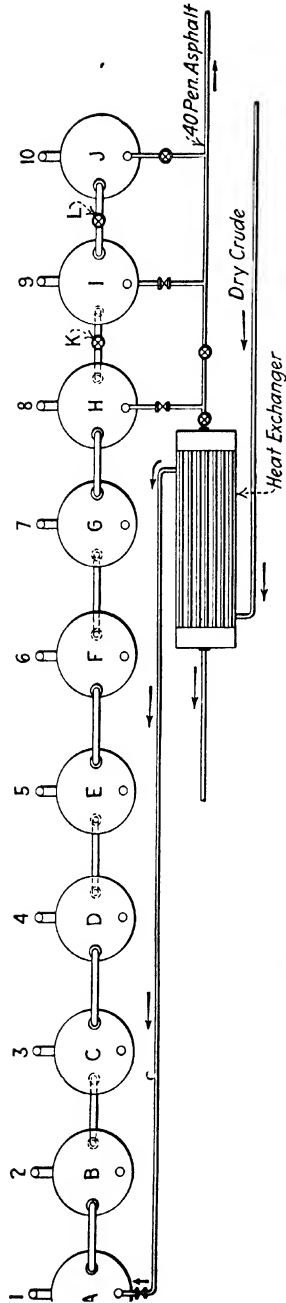
[1] 204° C.

Fig. 25.—Battery of continuous stills for reducing California crude oil.

coils, while the top of the last tower delivers into a separate coil. This arrangement provides for only four crude distillates and these may be represented by light naphtha, heavy naphtha, burning oil and lubricating distillate. The burning oil is collected separately from the light and heavy naphthas, while the gas oil, light and heavy lubricating oils may all be collected together and separated subsequently. The towers may or may not be provided with a go-back, but in case they are so equipped, this is operated but very little because cracking takes place so readily that the continued operation of refluxing would injure the distillates and lead to the production of too much coke. As shown in Fig. 24, which represents a one thousand barrel still, manholes are provided at either end and two manholes are situated on top of the still. It is customary on account of the large percentage of coke produced to charge only 750 barrels at a time. This will result with many Mexican crudes in the production of, say, 10 to 18 inches of coke on the bottom of a still at the end of a run. Before opening the manholes a jet of steam is used to blow hydrocarbon vapors out of the still and when the latter is sufficiently cooled the coke is removed by breaking it up and shoveling out. The purpose of the manholes on top of the still is to provide a better circulation of air during this operation of removing coke. The crude distillates obtained as mentioned are then given chemical treatment and steam distilling. With some Mexican crudes

twenty per cent of light naphtha may be obtained by this simple coking process.

In connection with the coking of some Mexican crudes it is a fact, not generally known, that toward the end of a distillation and as the coking period approaches, there is a considerable evolution of gas as though coke yielding substances suffered sudden decomposition previous to and during their pyrogenetic breaking up. Suitable provision must therefore be made to take care of this large volume of gas; in other words the receiving tanks connected with the top of the last tower on the still, in case towers are used, should be provided with a tail gas pipe of ample diameter, say 6 inches or thereabouts, and this pipe should lead to a gasometer or series of gasometers whose capacity is sufficient to take care of all the gas produced.

In the case of many asphaltic oils, particularly California oils, it is often customary to distill these oils continuously so as to obtain a residue of asphalt of about 40 to 50 penetration. Figure 25 shows diagrammatically a battery of 10 stills for making asphalt. These stills may be connected as shown so that the oil travels from the front end of one still to the opposite end of the next consecutive still in the series. This has the same effect as though the stills were connected together end for end. In the arrangement shown in Fig. 25 the last two stills I and J act essentially as reservoirs for the asphalt. Thus the reducing operation is continued until these stills become well filled and then by closing the valve K, H becomes the last still in the operating battery and while the stills I and J are being emptied of their contents the distilling operation is not disturbed, inasmuch as asphalt is continuously being pumped out of still H. The heat exchanger shown preheats the dry crude on its way to the first still in the battery. For the production of asphalt free from carbonized matter or " carbenes," as they are called, distillation is aided as much as possible by the introduction of live steam.

CHAPTER IV

REFINING METHODS, SULPHUR REMOVAL, CHEMICAL
TREATMENT, DISTILLATION

Among those phases of petroleum refining which have offered the greatest latitude for the application of chemical and chemical engineering invention and development, the desulphurization of sulphur containing oils and the removal of unsaturated hydrocarbons and other chemical substances, whose reactivity makes their presence undesirable for the uses to which petroleum products are at present usually applied, occupy a prominent place.

The partial practical solution of the desulphurization problem has resulted in increasing the supply of petroleum products by rendering available large deposits of oils, the fractions of which, until they are submitted to a desulphurizing treatment, are of little value.

The methods that operators and inventors have employed to attack this problem may conveniently be divided into two main classes, that is, treatment in the vapor phase, which usually consists in passing the oil in a state of vapor through or in contact with chemical substances calculated to effect a specific action on the organic sulphur compounds, and secondly methods which are confined to the liquid phase, for example, agitation of the sulphur containing fraction with agents such as sodium plumbite.

The liquid phase methods seem to have outlived or overshadowed those which are characterized as vapor phase methods. Whether this is a matter of convenience or of real chemical merit is a matter that may be questioned. This chapter endeavors to show the course which effort has taken in desulphurizing processes and methods.

The removal of unsaturated hydrocarbons and other reactive bodies holds at least as much interest as desulphurization. Present and past economical conditions and the present status of the chemical industry has limited large scale operation very largely to the use of sulphuric acid for this purpose. Other methods have been proposed, intended to represent improvements over the use of sulphuric acid, and while many of these methods undoubtedly accomplish from a chemical standpoint what they set out to do, many of them are not commercially employed on account of the expense of the necessary procedure. Refining with liquid sulphur dioxide, for example, while it has met with

some success in Germany, Austria and Italy, has, so far as is known to the authors, found little commercial application elsewhere. •Recognizing however that it is not improbable that new developments in refining methods may lead to the commercial application of chemical reagents other than sulphuric acid and caustic soda, there is recorded here the work of those who have sought to improve upon past and present methods as well as a description of current practice. The description is necessarily limited in general to those distillates from which it is possible to produce naphtha or gasoline.

Desulphurizing

J. Fordred [1] refines oils derived from coal, shale or peat by an initial treatment with caustic soda and a subsequent treatment with sulphuric acid. The alkaline and acid sludges are then mixed, treated with water and steam, sodium sulphate recovered and the hydrocarbon product of the combination of the acid and alkaline sludges isolated. The original hydrocarbon oil thus refined is further brightened by filtration through fuller's earth.

C. C. Parsons [2] proposes passing the vapors from an oil still through a mass composed of a mixture of charcoal and oxides of iron or calcium, under reduced pressure, in order to purify the oil, that is, deodorize and improve the burning qualities. Distillation of the oil with superheated steam is recommended.

A. T. Schmidt [3] proposed using much less sulphuric acid in refining distillates than was the current practice and to substitute a treatment with sodium " hyposulphite," in acid solution. It was said that this treatment had a good deodorizing and decolorizing action.

To the oil in the still is added a sulphite or hyposulphite of any metal which will not discolor the oil, for example, hyposulphite of soda. In general, there will be sufficient water present in the still to dissolve the chemical, but if there is not, then sufficient water may be added to the hyposulphite to bring it to a liquid condition before it is introduced. The distillation is then conducted in the usual manner, and the distillate obtained is removed to the agitator, where it is first treated with ordinary commercial sulphuric acid in about the proportions of one and one-half ($1\frac{1}{2}$) carboys of acid to every one hundred barrels of oil, to partially deodorize the oil, and to set free carbonaceous and coloring matters, which are allowed to settle, and the sediment removed. As soon as the matters set free by the first portion of acid have settled, the oil is treated with weaker acid, using about one-half carboy of acid to the hundred barrels of oil, and diluting the acid by the addition of water in about the proportions of one part water to two parts acid, by volume, the mixture being allowed to cool

[1] U. S. Patent 54,267, April 24, 1866.
[2] U. S. Patent 88,978, April 13, 1869.
[3] U. S. Patent 164,694, June 22, 1875.

before it is used, and the oil being agitated at the time the mixture is introduced.
The object of this treatment is to throw down all the coloring and foreign matter
which is still held in suspension, though set free by the first acid treatment. After
the distillate has been treated as above, it is washed in a bath having a hyposulphite
or hypophosphite in solution, preferably hyposulphite of soda, in about the pro-
portions of one pound of hyposulphite to forty gallons of water. The object of this
washing is to dissolve and carry off any coloring matter that may yet remain, and
also a portion of the free acid, enough of the acid remaining to unite with the hypo-
sulphite and liberate sulphurous acid, which, it is said, will bleach and deodorize the
oil. The oil is then subjected to a final washing with clear water, and neutralized
with an alkali as usual. The proportions given for the acid and water, and salt
and water solutions, are those which have been found to be serviceable. Schmidt
does not offer the method for the purpose of refining gasoline, but for the treat-
ment of hydrocarbon oils, generally.

Pitt [1] superheats oil vapors in the presence of metallic iron or copper
to effect desulphurization.

J. A. Dubbs [2] desulphurizes sulphur containing oils such as Lima
oils by heating the crude oil and blowing through it a stream of gas rich
in hydrogen. It is stated that if the crude oil is distilled without pre-
liminary treatment, carbon sulphides are formed which are relatively
difficult to destroy; that if, however, the crude oil is treated with
hydrogen before distillation, the sulphur is removed from the oil in the
form of hydrogen sulphide.

Frasch [3] finds that in distilling sour oils in the presence of oxide
of lead that this oxide is active at comparatively low temperatures and
so removes the " skunk " compounds from the lighter portions of the
oil, but that at higher temperatures it becomes inactive (owing to re-
duction). Copper oxide, on the other hand, acts in the reverse manner,
being more active at the higher than at the lower temperatures. One
of Frasch's " desulphurizing compounds " consists therefore of a mixture
of lead oxide and copper oxide. In order to increase the active surface
of these oxides they are also mixed with an inert refractory material,
iron oxide for example. The method of preparation of the desulphuriz-
ing compound consists in adding a mixture of the oxides of copper,
lead and iron to a " sour " burning oil distillate, distilling off the larger
portion of the charge in a cheese-box still with chain drag and roasting
the residue (after washing out excess oil with naphtha). This yields
the mixed oxides in a very finely divided active state. (Frasch states
that lead and copper oxide dissolve in sour oils to a certain extent.)
The resulting roasted mass is then used to desulphurize sour oils by
heating the latter and distilling them in the presence of the " copper

[1] U. S. Patents 379,492, March 13, 1888, and 411,394, Sept. 17, 1889.
[2] U. S. Patent 470,911, March 15, 1892.
[3] U. S. Patent 500,252, June 27, 1893.

(and lead) compound." Oil vapors may also be passed through such a specially prepared compound, heated to a suitable degree.

According to U. S. Patent 448,480, Mar. 17, 1891, Frasch preferred to pass the vapors from the distillation of sour oil through an agitated body of oil containing a mass of metallic compound (lead, copper, etc.), dissolved and suspended in sour oil.

Cazin [1] proposes to pass "sour" oil through a series of tall cylindrical vessels containing solutions of salts, alkalies and acids, intended to remove malodorous compounds. The aqueous solution or acid flows down through the vessel and oil rises upwardly through the aqueous liquid, collects on top of the latter and flows into the next purifier in the series. Figure 25a shows one of the purifying units. Dilute but not strong sulphuric acid, alkalies, salts of heavy metals and suspended oxides of copper, mercury and other heavy metals are mentioned as the purifying solutions used. Apparently the method was intended to operate continuously.
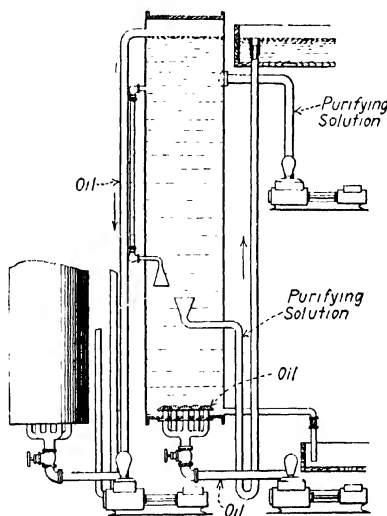

Fig 25a. — "Treating" apparatus proposed by Cazin.

The following substances were suggested as the cause of the bad odor:

Ethyl sulphate	Methyl sulphonic acid
Methyl sulphate	Methyl mercaptan
Methyl sulphide	Ethyl mercaptan.

Hans A. Frasch [2] treats oil with chloride of lime suspension to effect deodorization. Sulphuric acid treatment follows to remove unsaturated bodies and then a treatment with sodium plumbite. The latter reagent, it is said, is used only to remove chlorine compounds.

C. Lossen [3] believes that hydrocarbons belonging to the acetylene series have much to do with the bad odor of crude Lima and Canadian oils. He treats the oil with one-half to two per cent of cuprous oxide at about 120° C. (248° F.). It is stated that the odor was removed

[1] U. S. Patent 400,633, Apr. 2, 1889.   [2] U. S. Patent 525,811, Sept. 11, 1894.
[3] U. S. Patent 537,121, April 9, 1895.

but that the sulphur was not attacked. This is said to indicate that the sulphur compounds were not the cause of the bad odor.

Frasch[1] states that "Standard White" distillate when treated and then distilled gives off sulphur dioxide, indicating an oxidation by sulphuric acid during distillation, showing in turn that the alkali wash did not remove all acid. This difficulty was overcome by distillation in the presence of lime.

Frasch[2] passes the vapors from sour oil stills through a rotating drum containing a desulphurizing mass. The object of the rotation is to cause an abrasion of the surface of the particles of the mass, removing coatings of sulphide and thus preserving an "active" surface.

Adolf Kayser[3] proposes to improve low grade oils, i.e., oils containing large percentages of sulphur or smoky hydrocarbons, or both, by treating the oil in the vapor state as it emerges from the still, with carbon monoxide at a temperature of about 200° C. (392° F.) and at atmospheric pressure in a series of tubes situated between the still and the condenser. A subsequent treatment of the distillate (usually kerosene) with sulphuric acid is stated to yield an oil possessing excellent burning qualities. The formation of carbonyl sulphide (COS) is suggested as an explanation of the mechanism of the chemical reaction.

T. F. Colin and **Otto Amend**[4] are of the opinion that the removal of sulphur from petroleum is contingent upon oxidation of the sulphur; that successful removal of the latter takes place if it is oxidized by a strong oxidizing agent. They depart from the use of precipitating agents, like sodium plumbite, for example, and make use of the principle that if chlorine gas is passed into a sodium hydroxide solution containing an oxygen-carrier, such as manganese, cobalt, nickel, copper or iron, the hypochlorite is decomposed into chloride and oxygen, without the production of free chlorine.

In order to insure the production of oxygen alone without free chlorine, a catalytic agent which acts as an oxygen-carrier is used, preferably a salt of a metal which forms two or more oxides, which by oxidation or reduction, respectively, easily pass from one state of oxidation to a higher or lower state. Suitable salts for this purpose are the nitrates of manganese, cobalt, nickel, copper, and iron. It is necessary also besides this catalytic agent to have the solution distinctly alkaline in order to prevent the formation of free chlorine, and though this can be assured by the addition of a caustic alkali to the solution it is generally unnecessary to make this addition, as the solution of the hypochlorites of the alkaline metals or alkaline earthy metals usually contain a sufficient excess of alkali. The third important condition is the introduction of the chlorine in such a way that there shall be at no time any excess of the latter present—i.e., the hypochlorite solution must be allowed to run into the

[1] U. S. Patent 561,216, June 2, 1896.   [3] U. S. Patent 640,918, January 9, 1900.
[2] U. S. Patent 622,799, April 11, 1899.   [4] U. S. Patent 723,368, March 24, 1903.

oil very slowly and gradually (during the whole time necessary for agitation) and only as fast as the catalytic agent can react upon it. In order to insure this result, the oil is first treated with a strong solution of caustic soda, the solution having a specific gravity of approximately 1.4 to 1.5 to neutralize and eliminate acids, phenols and similar bodies. After settling, this alkaline sludge is drawn off, and the oil is ready for the actual sulphur treatment.

In order to effect the necessary oxidation of the sulphur in the oil the crude petroleum or distillate is agitated with a solution of sodium or calcium hypochlorite (bleaching powder), to which has been added a very small quantity of manganous nitrate. This manganous salt by interaction with the alkali and hypochlorite present is converted into manganese dioxide, which gives up its oxygen to the sulphur compounds of the hydrocarbons, itself being reduced and then again reoxidized by the hypochlorite, and so on. The direct addition of manganese dioxide (MnO_2) to the oil mixture might be used; but it will not be as effective, because the manganese dioxide, when precipitated in the mixture, as described, will exist in a much finer state of subdivision, as powdered manganese dioxide is not as finely divided as the precipitate produced in the solution by neutralization and agitation. The agitation is done by means of compressed air. This helps the oxidation and also carries away any free chlorine that may be present; but under these conditions no appearance of any free chlorine can be detected either by the sense of smell or by observing fumes with ammonia. The reaction above described takes place more easily at a somewhat elevated temperature, and therefore in cold weather the oil ought to be warmed. A temperature of about 40° C. is favorable; but satisfactory results are said to be obtained at a temperature of about 15° to 20° C. When the nitro-prusside test shows that all the sulphur has been oxidized, agitation is stopped to let the fluid settle, and the lower alkaline liquid is drawn off. Nitroprusside of sodium gives a red color with sulphides in alkaline solution; but when on application of a drop of an aqueous solution of nitro-prusside of sodium to a drop of the treated petroleum made alkaline with a drop of sodium ethylate dissolved in alcohol there is no appearance of any red color, it indicates that the oxidation of the sulphur in the petroleum has been completed.

The quantity of the hypochlorite to be used depends upon the amount of oxidizable sulphur present in the oil. It has been found that if the oil contains, for instance, 0.3 per cent of sulphur, it requires about 0.2 per cent of chlorine for its oxidation, and if the amount of sulphur in the oil and the amount of available chlorine in the hypochlorite solution are known, the proper quantity of the hypochlorite can be easily determined; but it may be pointed out that a slight excess of the hypochlorite will cause no harm.

Some hypochlorous acid (or its salt) will remain suspended or dissolved in the oil, and this must be removed or destroyed. . This is effected by treating the oil with a reducing agent. To the still slightly alkaline oil is added a solution of a salt of a metal which has two or more states of oxidation, each of which easily passes into the other, so that it can act as a reducing agent. For this purpose ferrous sulphate (copperas), manganous sulphate, ferrous and manganous nitrates, ferrous and manganous chlorides, ferrous and manganous acetates, or sodium plumbite are recommended. As ferrous sulphate (copperas) is very effective and cheap, this salt is preferred. A solution of copperas added to the oil containing chlorine and agitated with it for a little time will interact with the chlorine so as to form ferric chloride, which is harmless in the mixture.

If the methods above described have been followed carefully, the oil or distillate is now rendered free, it is said, from refractory compounds. The total sulphur

has been reduced to about one-half the original quantity, and what remains is in a form which submits to the usual acid treatment of petroleum distillates. A little " doctor " — i.e., sodium-plumbite solution — will show that all hypochlorous acid has been decomposed. As long as any of this latter is present sodium plumbite will turn black from the formation of lead peroxide. After letting the oil stand for a little while to settle, drawing off the aqueous liquid, and washing the distillate a couple of times with water, the oil is now ready for the usual treatment with sulphuric acid, alkali, and water.

These investigators use a very dilute hypochlorite solution.' For example, two hundred grams of kerosene were taken, and given the following treatments:

First, This distillate was washed with about five cubic centimeters of a strong solution of caustic soda in order to neutralize acids, phenols, etc., and the resulting alkaline sludge was separated.

Second, Fifty cubic centimeters of a solution of sodium hypochlorite were now added drop by drop. This solution was strongly alkaline (and therefore needed no addition of caustic soda) and contained 0.48 grams of available chlorine in one hundred cubic centimeters of the solution, or a total of 0.24 grams chlorine to two hundred grams oil — 0.12 per cent chlorine. To this was added one drop of a weak solution of manganous nitrate, as a catalytic agent, and the liquid was agitated by means of an air-blast for one hour while the hypochlorite was dropping in. At the end of that time the sodium nitro-prusside test showed (according to Colin and Amend, loc. cit.) the absence of sulphides in the hydrocarbons. The temperature of the room was about 17° centigrade.

Third, After allowing the liquid to settle and drawing off the alkaline solution the oil was washed four times with water.

Fourth, Assuming as a very improbable maximum that one-eighth part of the chlorine previously added still remained in the oil, twenty cubic centimeters of a copperas solution containing 0 2 grams of solid ferrous sulphate were added and the liquid agitated with an air-blast for twenty minutes. At the end of that time a test of a small portion of the oil with sodium plumbite showed that the plumbite did not turn black by the formation of PbO_2, thus proving the absence of hypochlorous acid. The liquid was settled and the iron solution drawn off.

The oil was then treated with the usual quantity of sulphuric acid and finished by washing with water and alkali.

The result was stated to be an oil of good color, standing the usual test with sodium plumbite, free from manganese and iron, and containing (as shown by the combustion test) a mere trace of chlorine and sulphur in quantity sufficiently low for commercial purposes.

Clarence I. Robinson [1] finds that sulphuric acid of ninety-eight per cent sulphuric monohydrate and above has a much more pronounced action on the sulphur compounds contained in the burning oil fraction [300° to 550° F. (149° to 288° C.)] of Lima (Ohio) and similar oils (e.g., Ontario, Canada) than acid of lower strength.

The burning oil fraction of Lima petroleum after treatment with 66° sulphuric acid in the usual way is stated: (1) to have a refractive

[1] U. S. Patent 910,584, Jan. 26, 1909.

index of 1.4400; (2) to contain not less than 0.2 per cent sulphur; (3) to turn a pronounced canary yellow on the addition of sodium plumbite solution and, (4) that by agitation with ninety-eight per cent sulphuric acid (0.3 pound 98 per cent acid to one quart of oil) the sulphur content is reduced from about 0.225 per cent to below 0.1 per cent.

It is also stated that the proportion of ninety-eight per cent acid needed to effect desulphuration depends largely upon the initial temperature at which agitation of the oil and acid is carried out.

It is said that by operating on Lima oil in the form of burning oil (kerosene) distillate (a) at about or below 38° F. initial temperature, a desulphuration to give a marketable burning oil (kerosene) can be effected with only about a third of the 98 per cent sulphuric acid needed to effect the same desulphuration at about 60° initial temperature; (b) that by operating at temperatures between about 38° F. initial and about 60° F. initial an equal desulphuration demands more and more acid until a temperature is reached at which substantially the same proportion of 98 per cent sulphuric acid is needed as would be required at about 60° F. initial; (c) that the increase in acid demanded for a given rise in temperature above about 38° F. initial becomes larger and larger as 50° F. initial is approached, so that the difference between about 38° F. initial and about 44° F. initial is not so great as between about 44° F. initial and about 50° F. initial, and this in turn not so great as between about 50° F. initial and about 56° F. initial, and (d) that the amount of desulphuration at about or below 38° F. initial and at any temperature between the latter and about 60° F. initial can be increased or decreased by using a larger or a smaller proportion of 98 per cent sulphuric acid, although it is believed that for a given stock and a given stronger acid there is an irreducible minimum, or, in other words, a certain sulphur content which cannot be reduced by using an increased proportion of the acid.

By treating the above mentioned uncracked stock with 98 per cent sulphuric acid at about 38° F. initial, followed by re-running, by a subsequent light treatment with sulphuric acid and alkali, and by steam stilling, finished burning oil (kerosene) is obtained with not exceeding $\frac{1}{10}$ per cent of sulphur, by using the 98 per cent acid at the rate of twenty pounds to the barrel of stock treated.

It is stated that there is no advantage, or at least none commensurate with the increased cost of cooling, in reducing the initial temperature of the stock below 38° F. as approximately the same desulphurizing effect per pound of 98 per cent or other high strength acid is obtained at lower temperatures. The following table shows the amounts of 98 per cent sulphuric acid to the barrel of stock which have been found to be needed to make a finished burning oil (kerosene) of $\frac{1}{10}$ per cent sulphur from the uncracked stock by treating it with acid at different temperatures at about and above 38° F. initial and then re-running the so treated stock and giving the re-run distillate a light treatment with sulphuric acid and alkali followed by steam stilling to remove the naphtha:

At about 38° F. initial . . . . .20 pounds
At about 44° F. initial . . . .25 pounds
At about 50° F. initial . . . .37 pounds
At about 56° F. initial. . . . . .54 pounds

The explanation of the ability of a smaller proportion of 98 per cent or other high strength acid, when applied to Lima oil at about or below 38° F. or at other tem-

perature below about 60° F. initial, to accomplish the same desulphurizing effect as a larger proportion of the same acid, when applied to the same stock at about 60° F. initial or at any lower temperature (above 38° F.) and also above that at which the smaller proportion of acid is used is thought to consist in the fact that the affinity of 98 per cent or other high strength acid for the sulphur compounds of Lima oil is diminished by such decrease in temperature less than its affinity for the unsulphured hydrocarbons of Lima oil is diminished. The chemical energy of the 98 per cent or other high strength acid is believed to expend itself, at all the temperatures both upon the sulphured and the unsulphured compounds; but the ratio in which it acts upon them, respectively, is different at the different temperatures; and the larger proportionate expenditure is upon the sulphur compounds at the lower temperatures. But, whatever the explanation, an equal desulphurizing effect is produced, it is said, by a smaller proportion of acid at the lower temperature; and there is less destruction of useful unsulphured hydrocarbons by the smaller proportion of the desulphurizing acid and also less injury by it to the color of the oil after re-running.

In desulphurizing the uncracked stock, the naphtha driven off in the steam stilling should have a sulphur content not exceeding $\frac{1}{100}$ of one per cent. A naphtha cut can also be desulphurized apart from the burning oil (kerosene) hydrocarbons; although it is considered ordinarily more advantageous to desulphurize them together and afterwards to separate the desulphurized naphtha from the desulphurized burning oil (kerosene).

It is also recommended to first give the kerosene a treatment with copper oxide and then to treat the distillate with ninety-eight per cent sulphuric acid. In this way the proportion of ninety-eight per cent acid necessary is much reduced, say, down to ten pounds of acid to the barrel. It is also believed advantageous, it is said, to separate the light from the heavy ends of the kerosene cut and the cracked from the uncracked distillates and to treat these cuts separately with the acid stronger than 66° Bé.

P. A. and **E. A. Starke** [1] purify hydrocarbons of the general formula C_nH_{2n+2} by passing them over a catalyst consisting of a mixture of an alkaline earth, an alkali, and a metal of the iron group, at a temperature between 1000° F. (about 540° C.) and 1600° F. (870° C.). Nitrogen compounds are separated and a mixture of hydrocarbons and aromatic compounds left, from which the latter are separated by cooling and subjecting to a pressure of 500 pounds per square inch. The remaining gas is said to be improved in heating and illuminating power.

W. O. Snelling [2] states that sulphur in combination with the light hydrocarbons in naphtha and burning oils may, by heating with a heavy unsaturated or " cracked " oil, be purified of its sulphur content,

[1] J. S. C. I., 1917, 77; U. S. Patent 1,206,156, Nov. 28, 1916.
[2] U. S. Patent 1,215,732, Feb. 13, 1917.

the sulphur becoming detached from the lighter hydrocarbons and reacting with the heavier oils. It is said that the sulphur remains permanently in combination with the heavy oil and that by distilling, the gasoline or burning oil comes over free from sulphur. The treatment with the heavy cracked oil may take place by refluxing at ordinary pressure or under pressure in the case of the more intractable sulphur compounds.

It is set forth that the heavy unsaturated hydrocarbons (which are said to react with low boiling sulphur containing hydrocarbons in such a way that sulphur is transferred from the low boiling body to the heavy unsaturated hydrocarbon) are best prepared artificially by cracking; for example, by passing crude oil or gas oil through hot tubes.

This is an important consideration, since it would indicate that, by cracking a "sour" burning or gas oil, and refluxing or digesting the products, one might obtain a naphtha free from sulphur.

By charging sulphur-containing oils like Kimmeridge (English) shale oils with sulphur dioxide and then distilling, **Hall**[1] observes that a very large proportion is converted into a form of sulphur that may be subsequently removed by the common methods in use for desulphurizing oils, whereas previous to the sulphur dioxide treatment, the sulphur compounds in the shale are very refractory.

Kimmeridge shale averages about 32 gallons of oil to the ton, but owing to the fact that the oil produced from it contains from 5 to 7 per cent of sulphur, the oil, it is stated, is practically useless as a fuel. Every known method of removing sulphur from oils has been tried with this oil, but the sulphur content, it is noted, has never been reduced below about 3 per cent except at excessive cost, whereas for an oil to be most serviceable as a fuel, it should contain less than 1 per cent of sulphur. Only a small amount of the sulphur can ordinarily be removed as hydrogen sulphide by distillation.

In Hall's process[2] the well known sulphur dioxide process for removing olefins and ethylenes from oils and for decolorizing oils is applied to Kimmeridge and like shale oils for the removal of the sulphur content. The oil is charged with sulphur dioxide gas while the oil is cold so that it will retain a large amount of gas. The oil so charged is then distilled, as a result of which a marked elimination of sulphur *in elemental form* is said to be obtained.

The distillate loses its nauseating odor, but nevertheless may contain a large amount of sulphur in a different state of combination. This sulphur is largely or wholly removed by any of the well known means of removing sulphur from oils such as, for example, the "Frasch" process. Any sulphur in suspension in the oil is separated by filtration.

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[1] British Patent 26,756, Nov. 21, 1913.
[2] British Patent 26,756, 1913; J. S. C. I. 1915, 167.

For this method it is claimed that the sulphur dioxide has an effect far greater than that of its simple combination with hydrogen sulphide (which would in any case be evolved) in that it apparently greatly assists the generation and discharge of hydrogen sulphide from the sulphur compounds of the oil. It appears that sulphur dioxide has a decomposing effect on the sulphur compounds, greatly increasing the amount of hydrogen sulphide evolved, a much more rapid discharge being obtained in this way than by merely distilling at the same temperatures.

E. V. Evans and the **South Metropolitan Gas Co.**[1] eliminate sulphur from tar oils by vaporizing the oil, mixing it with 5 to 10 per cent of hydrogen, or with a gas containing hydrogen, and passing the mixture over a heated catalytic or contact substance, such as nickel deposited on fireclay. Hydrogen sulphide is stated to be formed, and is removed. If the oil cannot be distilled, it is heated in contact with the catalyst. The hydrogen is then passed through or over it.

The following methods for desulphurizing Canadian oils are given by **Redwood.**[2]

" Owing to the large proportion of sulphur compounds (locally known as ' skunk ') which Canadian oil contains, the process of refining differed from that ordinarily employed in the United States. The agitators for refining the kerosene distillate held about 465 barrels, and with this quantity, strong sulphuric acid (two carboys) was agitated for twenty minutes. After withdrawing the tarry acid, agitation was repeated with a further quantity of seven carboys of acid, this operation being repeated twice if necessary, the agitation being continued for thirty or forty minutes, and the acid withdrawn after each operation.

" After settlement for an hour and withdrawal of the deposit, the oil was washed by fine streams of water, without agitation, for an hour and a half, or until a dark color produced by the acid treatment was removed. The water was then drawn off, and 10 barrels of caustic soda solution (15° Bé.) was added and the mixture agitated for fifteen minutes. The soda solution was in turn allowed to settle, and having been drawn off, the addition was made of 30 barrels of a clear solution formed by dissolving litharge in caustic soda solution of 18° Bé., the mixture being agitated for about six hours. By this means a considerable proportion of the sulphur was precipitated as lead sulphide and the oil was completely deodorized, but in order to remove the excess of lead, about 100 pounds of sublimed sulphur was added and agitation continued for another two hours. The oil was then allowed to settle all night."

[1] J. S. C. I., 1915, 1241; British Patent 22,147, Nov. 6, 1914.
[2] A Treatise on Petroleum, vol. II, p. 48, 1913.

" A large number of alternative processes have been proposed for removing the sulphur from Canadian and other similar oils, among which may be mentioned:

" (1) Distilling the oil over lead oxide, followed by refining with sulphuric acid.[1]

" (2) Dispensing with the use of sulphuric acid and treating the oil with a solution of copper sulphate, caustic soda and common salt, this being followed by digestion with flowers of sulphur.[2]

" (3) Passing the vapors from the still over heated iron or copper.[3]

" (4) Distilling the oil over lead oxide and washing the distillate with magnesium sulphate, the purification being completed by the usual treatment with acid and alkali.[4] Friedel and Crafts have proposed to treat the oil with aluminium chloride.[5]

" According to Tumski,[6] dilute nitric acid is sometimes employed instead of sulphuric acid for treating Canadian petroleum."

F. M. Perkin [7] states that there is a great variation in the sulphur content of oil from different regions. If combined with mineral matter in shale, etc., this portion will not pass into the oil on distillation, but if present in the " kerogen " or organic matter a considerable portion will appear in the distillate. The sulphur may be due to decomposition of vegetable or animal albuminous matter or, in case of very large contents of sulphur, may be produced by reduction of inorganic matter such as gypsum. The removal of sulphur compounds depends on their stability. They are generally distributed between all the fractions of the oil, but in greater proportion in the higher fractions, consecutive fractions from American crude oil showing the following percentages, 0.02, 0.10, 0.38, 0.41, 0.37, 0.37, 0.54. It is difficult to isolate these compounds owing to the proximity of the boiling points to those of the various hydrocarbons, and the only method of procedure, in some cases, it is said, is to combine the sulphur with some reagent, such as mercury chloride. Thiophene has been found in Russian and German oils, also thiophanes which may be looked upon as saturated thiophenes; and alkyl sulphides have been isolated from Canadian petroleum. Mercaptans seem only to have been noticed in Baku oils. Occasionally carbon bisulphide is found in petroleum. Unsaturated sulphur compounds may be removed by treatment with sulphuric acid, but under certain conditions the acid acts also on the unsaturated hydrocarbons and the method may be too costly. Moreover, sulphonic acids soluble in paraffin oils may be formed, giving off sulphur dioxide on heating, and actually adding sulphur to the oil. Sulphur in light naphtha

[1] **Frasch,** United States Patent 378,246, 1888.

[2] **Kennedy,** German Patent 43,145.

[3] **Pitt and Van Beck,** German Patent 45,958.

[4] **Gordon,** U. S. Patent 451,724, 1891

[5] Compt. Rend. (1878) (84), 1392.

[6] Technology of Naphtha (Russian), Moscow, 1891.

[7] J. Inst. Petrol. Tech. 1917 (3), 227–242; J. S. C. I., 1917, 702.

should be reduced to the lowest limit. Kerosene and lamp oils should be free from sulphur. Sulphur is allowable in greater quantity in fuel oils, but if present in unduly large quantities is said to cause pitting in the boiler plates and tubes. Attempts to desulphurize oil on a working scale appear to have originated in Canada in 1869. Oils from Ohio are desulphurized by cupric oxide. The volatile portion may be passed through the oxide, or the oil may be distilled to separate the light spirit from the heavier oil, each portion being then separately mixed with finely divided cupric oxide, agitated and heated in a still. The distillate is free from sulphur and the cuprous sulphide may be re-oxidised to copper oxide. **Blackmore** [1] is said to treat oil with calcium carbide, while in the **Edeleanu** process [2] liquid sulphur dioxide is used. On mixing the latter with a petroleum distillate, at about 5° C. (41° F.), two liquid layers are formed, the bulk of the sulphur compounds being found in the lower layer. Perkin does not consider the Edeleanu method suitable for the shale oils, particularly Kimmeridge shale oil, and is doubtful as to its suitability for heavy oils. In conjunction with **Lucas** and **Palmer**, he proposes to treat oil at high temperatures with gaseous ammonia, the temperature being sufficiently high to cause the ammonia to commence to dissociate. Oils treated in this manner are found to give off hydrogen sulphide. It is unfortunate, he notes, that the sulphur in the very extensive beds of so-called Kimmeridge shale is present in such a form that a very high percentage passes into the oil on distillation, the amount varying from 5 to even 8 per cent. The sulphur in this shale is said to be found in all the fractions and in spite of the evolution of hydrogen sulphide the amount in the distillate is not much less than in the crude oil. Kimmeridge shale oil would be of immense value if this sulphur could be removed, owing to the high yield of oil per ton of shale. The oil retains water in remarkable degree, one ton of shale giving 64.75 gallons of a crude oil containing 30.25 gallons of water and 3.74 per cent of su'phur.

The dry oil would probably contain over 7 per cent of sulphur. In retorting shales sulphur might be eliminated by: (a) removal in the process of retorting, (b) passing the oil vapors before condensation through a desulphurizing agent, (c) desulphurizing the oil by chemical means. There is no objection, it is said, to adding some material such as lime, and by previous treatment a larger yield of ammonium sulphate might follow. In the second case there is stated to be danger of carbonization, carbon being deposited upon the desulphurizing material, stopping its action. It is remarked that the third method presents considerable difficulty, owing to the risk of loss by action of the purifying agents on the oil itself.

[1] Fr. Patent 346,275; 1904; J. S. C. I., 1905, 127.
[2] British Patent 11,140; 1908; J. S. C., I. 1908, 974.

O. B. Evans,[1] referring to tests carried out at the Atlantic Refining Company for removal of sulphur from gases from the oil stills containing up to 8000 grains of hydrogen sulphide per 100 cubic feet of distilled gas, states that the method is applicable to the purification of illuminating gas. The installation consisted of 2 towers, 3 feet in diameter by 30 feet high, each filled with 136 cubic feet of 3-inch helical brick made of glazed earthenware. Each tower was placed above (and its lower end was sealed in) a 1500 gallon tank 7 feet in diameter by 6 feet high. The tanks were filled with a mixture of iron oxide, (Fe_2O_3) and water, which was pumped to the top of the first tower and sprayed down against an ascending current of gas. The foul oxide leaving the base of the first tower then was pumped into the top of the second tower and allowed to flow down against an ascending current of revivifying air. The revivified oxide was then recirculated through the first tower. In order to prevent the solid matter from settling, centrifugal pumps were used.

In order to condense and chemically treat petroleum distillates, **R. Fleming**[2] proceeds as follows:— Vapors such as are produced by cracking petroleum oils under pressure are condensed by treatment with water under pressure, as for example by an injector, against a suitable back pressure, the water, oil and permanent gases then being discharged into a tank or tanks for separation by gravity. The still vapors are led to an air condenser or dephlegmator to effect preliminary separation of tarry and heavy fractions. In the production of gasoline distillates, the cooling may be to about $300°$ C. ($572°$ F.) and vapor at about this temperature and under a pressure of 75 to 100 lbs. per sq. in. is passed under high velocity through an injector, where it is mixed with water, which effects condensation, washing and removal of impurities. Sodium carbonate, hydrated lime, litharge, lead acetate or caustic soda may be added to the water to act as desulphurizing and purifying agents. Free sulphur may be carried by the water to render soluble the insoluble sulphur compounds present. The apparatus used includes a separation chamber provided with an automatic relief valve for maintaining the desired back pressure on the condensing and separating system.

[1] Chem. Abs. 1919, 1380; Gas Record 1919 (15), 215-216; Gas Age 1919 (43), 475-476.

[2] Chem. Abs. 1920, 466; U. S. Patent 1,325,668, Dec. 23, 1919.

₋Purification by Colloidal or Adsorption Methods

Ujehely [1] employs the insoluble residue obtained in the manufacture of potassium ferrocyanide, known as " blacking " or " blackening," in order to deodorize and decolorize petroleum oils. The petroleum oil is dissolved, if necessary, in a light hydrocarbon and the resulting solution boiled with the purifying agent. It is stated that this " blackening " is composed of animal charcoal with iron, iron sulphide, potassium silicate and sodium silicate.

J. J. Johnston [2] purifies crude petroleum by distilling it in the presence of wood charcoal (in pieces about the size of a walnut).

Van Wyck [3] also advocates the use of carbon as a bleaching and deodorizing agent. He recommends a specially prepared charcoal made by carbonizing a pasty mixture of charcoal, chalk and soluble animal matter, such as blood or glue.

Lewis [4] advocates filtering benzine, naphtha or kerosene through a filter composed of a mixture of wood or coal ashes and charcoal, in order to deodorize the oil.

P. Vander Weyde [5] describes a filtering device intended to purify crude oil, which consists of a series of superimposed containers or buckets containing bone black. The oil passes through the bone black in each independent container.

Richter and **Richter** [6] believe that hydrocarbon oils (presumably unsaturated oils) in the presence of " active " carbon, are able to act as oxygen carriers, i.e., catalytic bodies, so that by the simultaneous use of such hydrocarbons with active carbon and an air blast or current, it is possible to remove malodorous constituents from naturally occurring and artificially prepared hydrocarbon oils (benzine, benzene and terpene hydrocarbons).

The oils to be purified are treated with the specially prepared carbon and then agitated with air at the ordinary temperature. It is stated that this treatment produces an oil which burns without a smoky flame and if employed in lamps yields no incrustation of nitrogenous carbon (cyanide). The carbon is prepared by mixing inflammable organic naturally occurring substances with chalk and clay and carbonizing the mixture.

[1] U. S. Patent 289,788, Dec. 4, 1883.
[2] U. S. Patent 31,982, Apr. 9, 1861.
[3] U. S. Patent 65,313, May 28, 1867.
[4] U. S. Patent 42,671, May 10, 1864.
[5] U. S. Patent 61,125, Jan. 8, 1867.
[6] German Patent 240,760, Klasse 120; Gruppe 1, May 13, 1910.

G. M. Saybolt[1] advocates the use of fuller's earth with which to treat light petroleum distillates (sp. gr. 850 and less) which have been washed with sulphuric acid. He is of the opinion that the use of an alkaline wash does not completely remove sulphonic compounds from the oil. By largely or wholly avoiding the use of the alkaline wash and substituting for it thorough agitation with fuller's earth it is said that a better quality of burning oil or naphtha is produced.[2]

Fuller's earth, supposedly a bisilicate of alumina, or bauxite, clay, or charcoal, either vegetable or animal may be used. Any of these substances, or a mixture of them, is pulverized and added to the acid-treated distillate and thoroughly agitated for about an hour. After such treatment and the settlement from the oil of the pulverized absorbent material, the oil is drawn off and will be observed to be deodorized, very much improved in color, and freed from sulphonic and other acids as well as from the separated tarry matter and other impurities. The distillate is then ready for the market and will be found, it is said, to be better and purer than oil refined from like acid-treated distillate by the ordinary processes. The proportion of fuller's earth to be used depends upon the proportion of sulphuric acid which was originally employed in treating the distillate. When 0.6 per cent of sulphuric acid of 66° Bé. has been used, 2.5 per cent of fuller's earth is used and as the percentage of acid is increased the percentage of fuller's earth is increased.

Hall[3] describes a method of separating heavy and light hydrocarbons by a method which depends on physical adsorption.

A heavy oil is agitated with a solution of a feeble alkali (e.g., lime water), using about 50 per cent of the oil and 50 per cent of a strong solution of the lime water. After the oil and lime water have been agitated together, there is added to the liquid an amount of sulphate of alumina sufficient to combine with all the alkali (say about 2 per cent of the weight of the oil) which produces a coagulation, a large amount of white curd-like substance being precipitated. This curd-like substance is then separated by filtration. From the remaining liquid which contains about 5 parts water to 4 parts oil, the water is extracted by settling and the oil mass left is found to have a much lower boiling point, it is said, than the original oil used. The precipitate thrown down is a finely divided flocculent deposit of aluminum hydroxide, which appears to have the characteristic of carrying with it some of the heavy hydrocarbons of the oil. By this method, it is stated the boiling point of an ordinary paraffin oil with a specific gravity of about 47.5° Bé. has been lowered from 140° C. to 60° C. (284° to 140° F.)

[1] U. S. Patents 565,039 and 565,040, Aug. 4, 1896.
[2] See also **Frasch** (above) U. S. Patent 561,216, June 2, 1896.
[3] British Patent 18,342, Aug. 12, 1913.

T. Hamilton [1] describes an unusual method for purifying petroleum and simultaneously separating it into light and heavy fractions without distillation. An emulsion of oil and brine solution is made and this is then allowed to drop through a pipe, thus being submitted to a sudden shock. It is said that the emulsion then partly breaks and that the lighter, purer and more volatile portions of the oil readily separate and may be decanted off or filtered.

J. C. Whitman [2] uses a filter bed of bog iron ore for filtering petroleum oil to effect cheaper and more rapid filtration than is attained with fuller's earth.

Removal of Unsaturated Hydrocarbons

Benjamin T. Brooks and **Erwin Humphrey** [3] believe that the refining of cracked gasoline constitutes a special refining problem. The foul odor of cracked gasoline is, it is stated, not due to olefins, but to sulphur compounds, nitrogen bases and traces of naphthenic acids. It has been found that very sweet, stable gasolines may be made by treating with a small quantity (not over six per cent by weight) of 85 to 90 per cent sulphuric acid, followed by washing with alkali in the usual manner and redistilling. This method of operating is said to be sufficient to remove thoroughly the most reactive and objectionable constituents, i.e., tar or resin-forming diolefins and malodorous compounds. It is observed that Hall endeavors to accomplish the same object by distillation through fuller's earth, and Justice [4] seeks to attain the same result by milder polymerizing agents, i.e., metallic chlorides such as zinc chloride or ferric chloride. In the interest of conserving gasoline, the shortage of which, it is noted, will undoubtedly grow more and more acute, it is recommended that the old sulphuric acid methods of refining should be discarded or modified, even if standards of quality heretofore the rule have to be modified and based solely upon efficiency during use.

The "neutral alkyl sulphates" left in motor spirit after refining with sulphuric acid are considered by Brooks and Humphrey to be one of the causes of the instability sometimes noticed in these products. The neutral esters rapidly decompose at 140° C. (284° F.) or higher temperatures, but decomposition also takes place slowly at ordinary temperatures, and causes the darkening of the oils on standing and the separation of a small proportion of a brown viscous layer containing

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[1] J. S. C. I. 1912, 324A, 977; U. S. Patent 1,018,971, Feb. 27, 1912.

[2] Chem. Abs. 1919, 2594; U. S. Patent 1,312,375, Aug. 5, 1919.

[3] J. Am. Chem. Soc. 1918, 952.

[4] British Patent 3572, 1914, J. S. C. I. 1915, 1004.

a little free acid and much resinous matter. It is recommended that spirit and kerosene refined with sulphuric acid be always subsequently redistilled.

Brooks and Humphrey [1] have made an extensive study of the action of concentrated sulphuric acid on olefins with particular reference to the refining of petroleum distillates. From this investigation the conclusion is reached that when refining motor spirits or kerosene containing olefins, by means of strong sulphuric acid, complete solubility in the acid at ordinary temperatures is attained only by those grades which consist practically entirely of the lower members of the olefin series, while other grades which yield oily layers insoluble in the acid do so either because the acid treatment is not carried sufficiently far, or because the spirit or kerosene contains a certain proportion of higher homologues of the olefin series, paraffins, naphthenes, or aromatic compounds. In such cases if olefins were present in the original oil, the residual oily layer always possesses an increased specific gravity and distillation temperature. But it is observed that the refined oils obtained by treating spirits or kerosenes with liquid sulphurous acid always possess lower specific gravities than the original unrefined oils from which they are derived. When refining by means of sulphuric acid, therefore, two separate actions take place concurrently according to Brooks and Humphrey; firstly the partial removal of the olefins from the spirits or kerosenes, thus tending to lower the gravities of the residual oils; and secondly, the polymerization of some of the olefins and the formation of neutral alkyl esters, both of which products pass into the refined oils, tending to raise both their gravities and their distillation points. The net result is that a rise of the specific gravity and of the distillation temperature takes place.

The analytical determination of the amount of olefins present in motor spirits and kerosenes by treatment with strong sulphuric acid is therefore not a quantitative operation, but may and does nevertheless possess a considerable technical value as an arbitrary test to assist in forming a judgment as to their origin. A closer approximation to the determination of the olefins in such hydrocarbons by treatment with sulphuric acid than is possible by the method ordinarily used, is to agitate the oil thoroughly with cold acid, separate the acid layer, wash the oily layer with water and then with an aqueous caustic soda solution and with water again, then dry the oil and distill up to the highest temperature at which the original oil distilled before treatment; any residue then remaining in the flask clearly consists, it is said, either of polymerized olefines or of neutral alkyl sulphates or both, and its volume

[1] J. Amer. Chem. Soc. 1918, 822; J. S. C. I. 1918, 361 A.

should be added to the other loss observed on treating the original oil with sulphuric acid.

Diolefins are considered to be sometimes present in spirits and kerosenes, especially those which have been obtained by cracking heavier oils at unusually high temperatures, such as 600° to 800° C. (1112 to 1472° F.). It is the presence of these diolefins which chiefly gives rise to the troublesome "gumming" from resin formation sometimes observed. Brooks and Humphrey, moreover, consider that it is the diolefins which, in contra-distinction to the olefins, give rise to tar formation when treated with sulphuric acid.

Refining methods based on the use of fuller's earth or the action of such mild polymerizing agents as the chlorides and sulphates of some of the heavy metals have recently been proposed.[1]

The refining of gasoline, naphtha, burning, lubricating and other oils' and simultaneous production of a commercial synthetic resin by the action of finely divided porous substances at an elevated temperature is described by **Leslie** and **Barbre.**[2]

Oil is charged into a digestor provided with reflux and ordinary condensers and the polymerizing agent is then added. The latter may be fuller's earth, kieselguhr, clay, charcoal, powdered coke or the like, in admixture with an alkaline substance such as calcium carbonate, weak acid salts of any of the alkali or alkaline earth metals. Alternate refluxing and distillation is employed, that is the charge is first boiled under reflux with subsequent elimination of some refined distillate. Refluxing is next employed at a temperature which is higher than in the case of the initial treatment under reflux on account of the elimination of the more volatile fractions. Alternate refluxing and distilling is then continued until the refining, that is polymerization of unsaturated hydrocarbons, phenols, organic acids, nitrogen compounds, sulphuric compounds and the like has proceeded to the desired stage. The final product is given a steam distillation which eliminates heavy oils, leaving a residue which on cooling is said to be a synthetic resin.

Hall[3] applies the continuous refining idea to his crude cracked gasoline. Fuller's earth is the refining agent. This is kept at a temperature somewhat above the boiling range of the highest boiling distillate contained in the gasoline to be refined say, a little above 200° C.

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[1] Allgem. Ges. für Chem. Ind. m. b. H. British Patent 3572, 1914; J. S. C. I. 1915, 1004; Report Soc. Chem. Ind. 1918, vol. III, 66.

[2] U. S. Patent 1,337,523, Apr. 20, 1920.

[3] Chem. Abs. 1918, 994; British Patent Application, Aug. 26, 1916; No. 12,100, Complete Accepted, Aug. 27, 1917; French Patent (Hall Motor Fuel, Ltd.) 483,231, June 13, 1917.

(392° F.). Hence the refining consists in the contact between the solid earth and the gaseous hydrocarbons. This refining process, in common with other continuous processes for refining gasoline, eliminates loss of light fractions. The method is also said to be effective in refining fatty acids and naphthalene.

In refining crude spirit by distillation alone or with fuller's earth, it has been found impossible, it is said, to distill the spirit without considerable loss of the low boiling fractions, *i.e.*, the most valuable portion of the spirit. In some cases this loss has amounted to as high as 30 per cent.

Fuller's earth, and particularly a variety of fuller's earth, known as floridine, when maintained at or above the temperature of the highest boiling point of the distillate required, acts on crude cracked spirit passed through the adsorbing substance in the form of a vapor, without fractionation, in such a way that an inodorous motor fuel can be obtained, it is stated, with practically no loss of the low boiling fractions.

The explanation of this result appears to be, Hall states, that when a crude spirit is distilled either with or without fuller's earth from a still, the low boiling fractions come over first and these cannot be condensed owing to the fact that insufficient condensable matter comes over with these gases to hold the gases and permit them to be condensed. According to the process described practically all the fractions of high and low boiling point come over together so that there is a sufficient amount of readily condensed product to hold and condense the gases.

In carrying out the process the spirit is heated so as to cause it to vaporize and the vapors produced are led through a number of columns of fuller's earth in succession, the fuller's earth being maintained at a temperature of about 200° C. (392° F.) by the arrangement of the columns of earth in an oil bath maintained at a constant temperature. The maintenance of the temperature may be secured by superheated steam. The spirit obtained by condensation of the vapors, so treated has lost the characteristic odor and color of " cracked " spirit. The fuller's earth becomes gradually less active and after a certain time loses its effect. The spirit may be preheated and preliminarily treated by passing it through a column containing coke and heated by the oil bath or even through a column containing Raschig rings, *i.e.*, rings of wrought iron similar in appearance to 1″ slips of bicycle tubing, which act as a very efficient dephlegmator and preheater assuring that the crude spirit up to the temperature desired is completely vaporized.

In Figures 26 and 27 a tank A is erected over a furnace B. Within the tank A are a series of six columns C^1, C^2, C^3, C^4, C^5, C^6, connected by a system of piping in such manner that the series of columns may be connected in any desired order and any column cut out at will. Of this series column C^1 is filled with Raschig rings and is always used as a dephlegmator and preheater, a cock being provided at the lower end of the column for the removal of any material in the spirit boiling at a temperature higher than that of the bath. The spirit is introduced near the bottom of column C^1 from a coil D of piping surrounding the column C^1, this coil being arranged to insure thorough heating of the spirit before its introduction into the column C^1. The columns C^2, C^3, C^4, C^5, C^6, are filled with fuller's earth and the spirit, in the form of vapor taken from the column C^1, is led through the pipe F to the column C^2. Owing to the low heat conductivity of the fuller's earth and in order to heat this material throughout the crude spirit gases are passed through a triform series of pipes F^1 to the lower end of the column and allowed to pass upward through the

fuller's earth and by way of the outlet pipe to the next column C^3 which is also provided with triangularly disposed pipe F^1 and so on to the next column in succession and finally to the outlet.

For a certain period of time column C^2 will deliver water white refined spirit, but after the end of this time the product from this filter is slightly tinged with
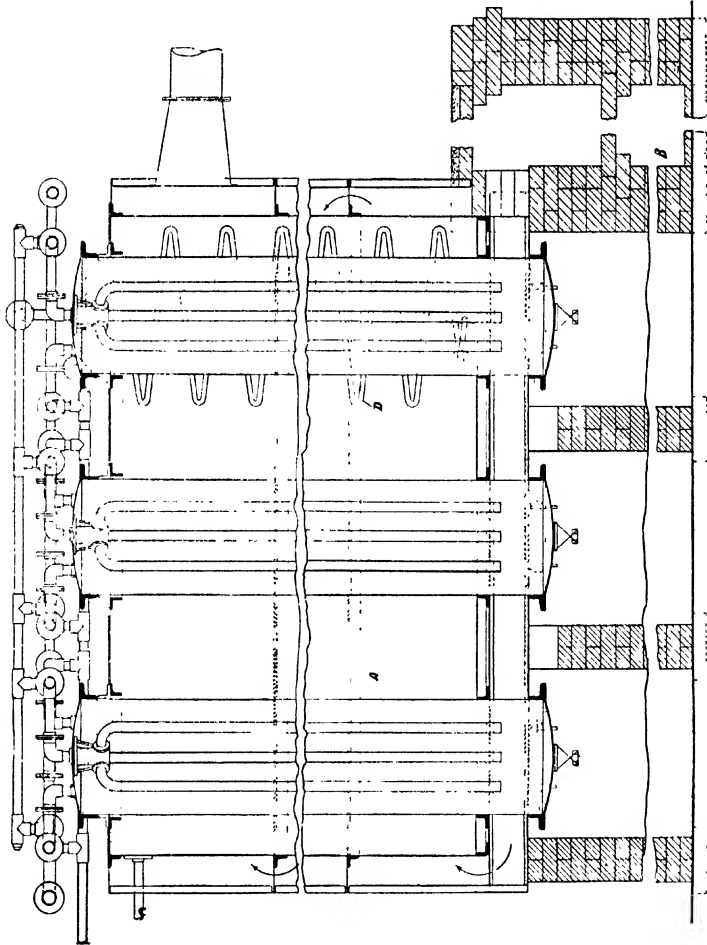

Fig. 26. — Continuous refining apparatus proposed by Hall (elevational view).

yellow. The gases are then passed through column C^3 which, only having a small amount of work to do, remains in an efficient condition for a very much longer period of time. When the column C^3 delivers slightly tinted spirit the column C^4 is included in the series, and, even when C^4 develops the same tint, the spirit issuing from column C^1 is still a great improvement on the spirit entering, proving that the fuller's earth is still doing good work. With the design of the apparatus shown, it
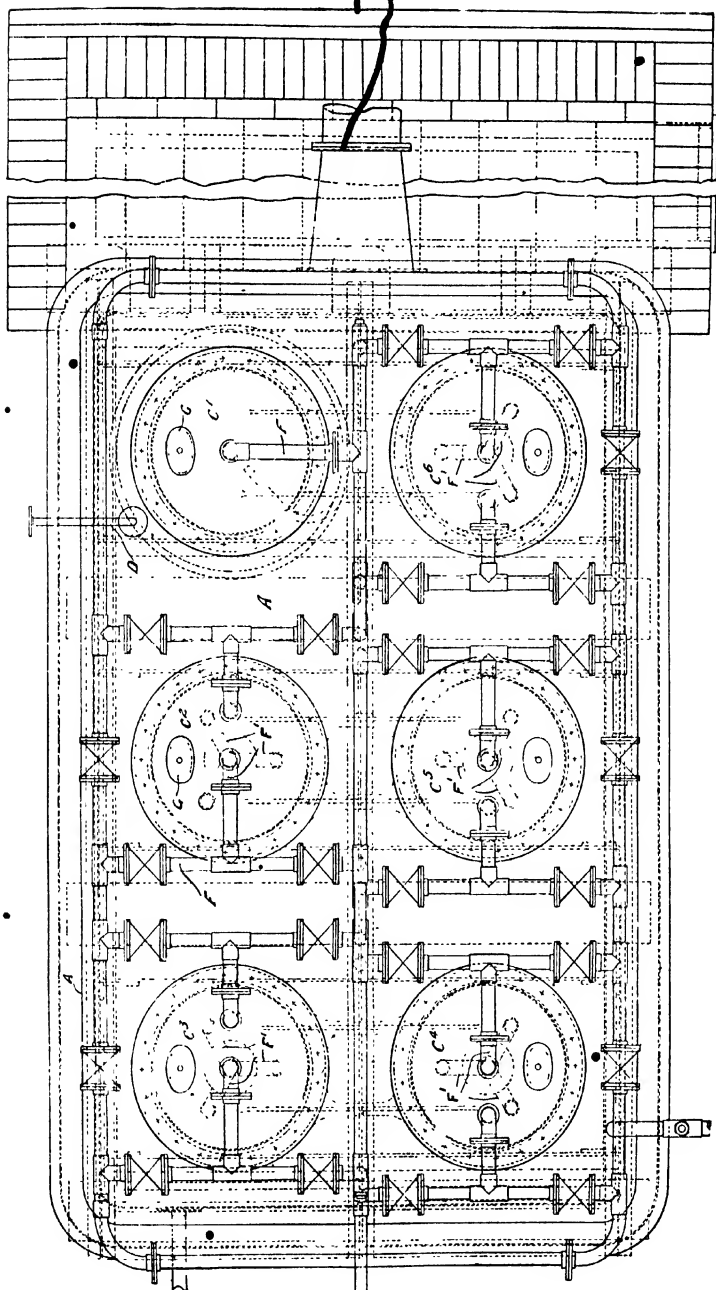
Fig. 27. — Continuous refining apparatus proposed by Hall (plan view).

is found that, when the column C^6 is started the column C^2 will have been used up and it will then be possible to expel the contents, fill it with hot dry fuller's earth through the manhole G and then allow it to rest until it is necessary for it to be drawn into the cycle of operations again. Between each column there may be a small test cock and a condenser so that, when the plant is in operation, colour tests may be made to determine the quality of the spirit passing through any one of the filters.

Each column is provided with a manhole G. The chemical condensation product produced by the action of the crude spirit on the fuller's earth is quite liquid at the temperature at which the bath is maintained, and during the distillation may be drawn away by means of the cocks provided at the bottom of the columns. By this method of distillation, the light and heavy portions distill over together and therefore any efficient form of cooling device is sufficient and the loss of the lighter fractions avoided. When the apparatus is once in operation the amount of gas required to keep the temperature constant is comparatively small. Gas fuel is used in the furnace shown, because it is one of the products of the cracking process and so easy to regulate in practice. As a maximum it is not necessary to use more than 20 pounds air pressure or a pump working at a maximum of 20 pounds per square inch to overcome the back pressure of the spirit passing through the refining apparatus. Girds (not shown) inside each column support the fuller's earth, so that the condensation product can drain away and be tapped off.

T. T. Gray [1] purifies volatile hydrocarbons by passing them in a state of vapor through a mass of porous material possessing absorbing powers such as fuller's earth at a temperature above the boiling point of the vapors, for the purpose of removing unsaturated compounds and other reactive compounds.

Frasch [2] treats Beaumont burning oil with alcohol to remove " smoky " hydrocarbons.

C. K. Francis and **D. G. Morgan** [3] describe a method for refining cracked distillates, by treating the material with a saponaceous mixture containing an excess of alkali and distilling the mixture. The treating solution may be formed of fat 2, caustic soda (NaOH) 0.3 and sodium carbonate (Na_2CO_3) 3 parts. Water white products are said to be obtained in this manner.

A. L. Thompsen [4] produces light distillates for use as turpentine substitutes by distilling petroleum at 95° to 110° C. (203° to 230° F.) in the presence of soda solution in the proportion of 3 parts soda and 300 of water to 100 parts of oil.

C. Ellis [5] observes the difficulty of obtaining a light colored or water white gasoline from cracked oil containing large amounts of readily oxidizable unsaturated hydrocarbons where strong sulphuric acid is

[1] U. S. Patent 1,340,889, May 25, 1920.
[2] U. S. Patent 951,272, Mar. 8, 1910.
[3] Chem. Abs. 1919, 2760; U. S. Patent 1,313,629, Aug. 19, 1919.
[4] Chem. Abs. 1919, 2276; British Patent 126,089, May 3, 1918.
[5] U. S. Patent 1,318,061, Oct. 7, 1919.

used for refining purposes. Not only is the strong acid itself discolored but its action imparts a dark color to the cracked naphtha. This is explained by the formation of gasoline soluble dyestuffs. Ellis refines cracked gasoline with dilute sulphuric acid, of say 40–70 per cent strength, the precise strength being found by control tests on the oil which is being handled. One form of treatment involves the use of about 5 per cent of sulphuric acid of fifty per cent strength. Suitable treatment of highly unsaturated gasoline with dilute acid followed by a " sweetening " with caustic soda and the customary water wash is said to result in the production of a stable, water white gasoline although it may still contain a large percentage of unsaturated hydrocarbons. Ellis also notes that gasoline suitably refined in this way and containing considerable percentages of unsaturated material is more responsive to the throttle when used in automobiles than a saturated gasoline of the same gravity (e.g., 54° Bé.). This is on account of its greater volatility, more rapid diffusibility, lower flash point, greater ease of ignition and apparently more effective combustion.

As regards the superior qualities of " cracked " over " straight " gasoline, when used in motors Hall (see chapter on Hall process) makes observations similar to those of Ellis.[1]

G. Egloff [2] states that estimates showed that approximately 70,-000,000 barrels of gasoline were used (in the U. S.) during 1917. In refining gasoline an average of one pound of sulphuric acid, 0.1 pound of sodium hydroxide and 0.75 barrel of water for washing are stated to be used per barrel of gasoline. This treatment means a loss of at least 1 per cent. Using the above estimate this would mean a loss of 700,000 barrels of gasoline, the use of 35,000 tons of sulphuric acid, 3500 tons of sodium hydroxide, and water for washing. The acid treatment increases the cost and is said to add little to the value of the product. The unsaturated hydrocarbons removed are stated to have greater driving power than saturated or paraffin hydrocarbons. There should be no objections to the use of gasoline with a slight color and odor; hence he affirms it should not be necessary to refine even cracked gasoline. Egloff maintains that conservation demands that gasoline should not be treated.

The burning oil fractions of Beaumont oil, according to C. I. Robinson [3] contain hydrocarbons characterized as " smoky." These bodies, it is said, can economically be removed by treatment with 98 per cent

[1] See also Ellis, U. S. Patent 1,318,060, Oct. 7, 1919.
[2] Chem. Abs. 1917, 3425; Oil and Gas J. 1917 (16), No. 11, p. 32; Chem. Met. Eng. 17, 156.
[3] U. S. Patent 968,692, Aug. 20, 1910.

sulphuric acid, whereas they resist action by ordinary 66° Bé. acid in the customary treating method. Further acid economy is said to result by distilling the oils (treated with 98 per cent acid) leaving a liquid residue of treated oil in the still.

H. T. Maitland [1] departs from the usual procedure followed in treating distillates with sulphuric acid. He subdivides or atomizes the acid in such a way that a definite weight of acid is given a very large, effective surface. This is said to result in an economy in the use of sulphuric acid,

It is stated that the action of the sulphuric acid (which is not miscible with the oil) upon the unsaturated hydrocarbons is largely, if not wholly, superficial. That is, the acid, when agitated with the oil, is divided into a large number of particles, many of which are quite large and which are quite visible to the naked eye; and these particles act, not to absorb or react with the impurities which it is desired to remove, but to catch them and hold them upon their surfaces. In other words, the impurities do not either combine with or penetrate the entire mass of the acid, and the effective action of a large portion of the acid is therefore lost.

Fig. 28. — Maitland's treating apparatus.

Concerning the application of the liquid sulphur dioxide method to the refining of naphtha and other distillates, **Moore, Morrell** and **Egloff** [2] have carried out an interesting series of investigations on the subject and come to the following conclusions:

(1) Naphthenes, which the literature states are insoluble, may be completely dissolved in sufficient quantities of the solvent.

(2) It has been found that, within certain limiting concentrations, (*a*) aromatics may be separated from paraffins or naphthenes, (*b*) olefins may be separated from paraffins or naphthenes, (*c*) aromatics and olefins together may be separated from paraffins or naphthenes, (*d*) naphthenes may be separated from paraffins. [3]

(3) The application of the liquid sulphur dioxide method to analytical work on oils is of importance since the separated unsaturated or aromatic hydrocarbons may be recovered and their identity proven by further physical tests. In sulphonation for olefins and nitration for aromatics these oils are lost. Moreover, naphthenes may be separated

[1] U. S. Patent 1,272,979, July 16, 1918.

[2] Met. and Chem. Eng. 1918, 396 *et seq.*

[3] The work of **Walden** (Ber. 1899 [32] 2862), **Edeleanu** (Bull. Am. Inst. Min. Eng. 1914 [93], 2313) and **S. E. Browery** (Pet. Rev. 1917 [36] 351, 385, 401) is noted.

from paraffins within prescribed limits, a fact that will appeal to the oil analyst.

(4) The application of the sulphur dioxide method to oil refining may prove of importance since the valuable aromatics and unsaturated hydrocarbons are recovered, the refined oil is purer than the acid method yields, and the sulphur dioxide may be applied and recovered in a continuous cycle

J. C. Black[1] treats oils with sulphur dioxide, under pressure. The products separate into two layers. The bottom layer is withdrawn and its gas pressure reduced, which causes it to separate into layers. The second bottom layer thus formed is removed and relieved of its gas pressure. The first and second top layers also are freed from absorbed sulphur dioxide, and then are mixed together and further freed from residual sulphur dioxide and the top layer mixture and second bottom layer are separately collected, the sulphur dioxide being reused in treating fresh crude oil.

Distilling and Fractionating Methods [2]

J. B. Grant and **A. Mason**[3] subject crude petroleum to an instantaneous vacuum distillation with the aid of steam. The oil is injected, by means of high pressure steam, into a heated retort in series with a surface condenser and vacuum pumps. A large yield of high grade illuminating oil is said to be obtained.

A. W. Wilkinson[4] uses gases such as carbon dioxide or monoxide, hydrogen, natural gas or light hydrocarbons in place of steam in distilling petroleum, in order to obviate the difficulties which, it is observed result from the persistent emulsions resulting from the use of steam.

Ragosin[5] uses a hydrocarbon gas, for example, benzol vapor, instead of steam, as an aid in the distillation of petroleum. He also employs dephlegmating " towers." Figure 29 shows two of these towers.

[1] U. S. Patent 1,164,162, Dec. 14, 1915.

[2] For a very exhaustive account of commercial refining and topping plants the reader is referred to a monograph on this subject by **J. M. Wadsworth.** (Bureau of Mines Bulletin 162, Removal of the Lighter Hydrocarbons from Petroleum by Continuous Distillation with a Special Reference to Plants in California, 1919.) Plants operated by the methods of **A. F. L. Bell, I. W. Fuqua, E. I. Dyer, Prutzman** and **Trumble** are described as well as the **Brea** and **Brown-Pickering** plants.

[3] U. S. Patent 339,545, April 6, 1886.

[4] U. S. Patent 145,707, Dec. 16, 1873.

[5] British Patent 1311 Jan. 18, 1898.

Frasch [1] removes naphtha from burning oil incident to raising the fire test of the latter. The still has a dephlegmating tower and a heat exchanger. The process is continuous. Low test distillate flows down
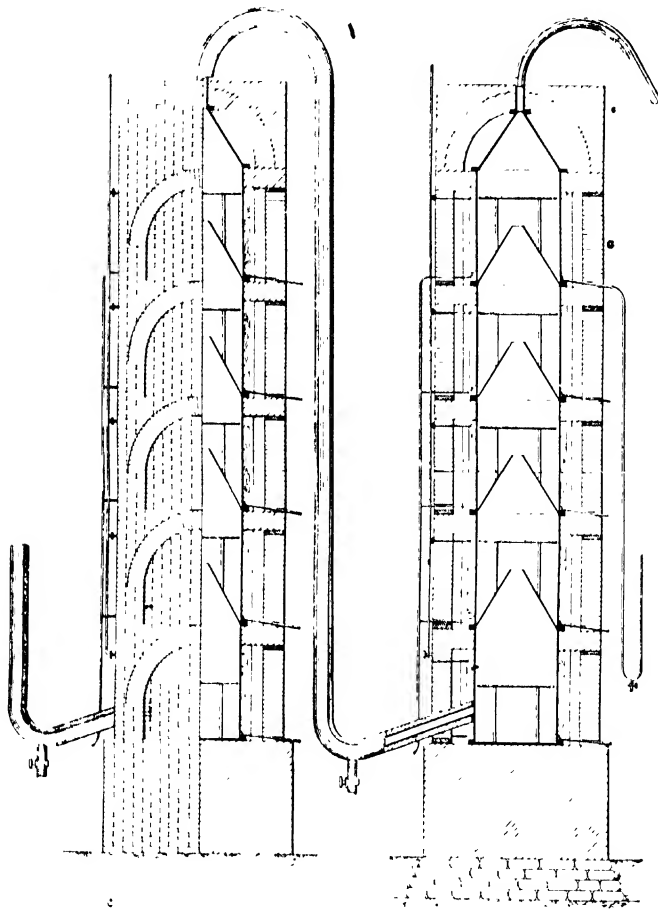
Fig. 29. — Dephlegmating towers, according to Ragosin.

in the dephlegmator in a stream counter to the vapors from the still, and steamed high test distillate is pumped out of the end of the still farthest from the dephlegmator. This high test distillate then

[1] J. S C. I. 1907, 464; U S Patent 845,456, Feb. 26, 1907.

passes through a heat exchanger through which low test distillate is passing on its way to the dephlegmator. The apparatus can be used equally well, with some modifications, for working up light or heavy naphthas or gas oil.[1] Its purpose is to effect a rapid volatilization of naphtha in such a way that any given volume of distillate being treated is subjected to heat for a very short time and is therefore much less apt to be darkened by exposure to heat than in discontinuous methods where a large volume of oil is exposed to heat for a relatively long time.

It is observed that in the fractionation of crude petroleum by distillation the operation can be so conducted as to give burning oil distillate, having as it comes from the end of the condenser the fire test desired, but in proceeding in this way prior to the recovery of this high-test distillate, there would be received a product too light to be burned in a lamp and too heavy for use as naphtha (benzine), yet containing desirable portions of burning oil and naphtha. It has been the practice, therefore, to commence the collection of distillate for burning oil while the more volatile constituents of the crude oil are still coming over, and to resort to a supplementary distillation to remove these constituents, or, in other words, to raise the fire test of the burning-oil distillate. The particular points at which the collection of this distillate shall begin and end and in what manner the distillation is to be conducted are determined by the judgment of the manufacturer, according to the character of the products which he is making and other considerations, and he may collect this burning oil distillate in fractions, one or more of which would be of the proper fire test as it came from the condenser and these could be mixed with the remainder of low fire test after this has been deprived of its more volatile constituents, but in practice all the distillate for the particular grade of burning oil being manufactured is collected or mixed together and subjected to the operation for raising the fire test.

In order to separate lighter oils from the burning oil fraction resort was first had to a partial distillation by fire heat in order to raise the fire test, but while this was effective in this regard, in using fire under the still the boiling point of the more volatile constituents was so high that a polymerization set in with an accompanying coloring of the distillate, which made the subsequent treatment with acid very difficult. In fact, some oils subjected to such supplementary fire distillation could not be made white at all. To remove this difficulty, the supplementary distillation for fire test was effected by steam, the distillate of low test being brought into contact with free steam. Various processes and apparatus have been proposed for such steam-stilling, but it is noted that the current procedure was as follows: The low-test distillate was placed in a large still, having a capacity in large refineries of from two thousand five hundred to four thousand barrels, and provided with steam coils, some of them closed so as to raise the temperature by dry heat and others perforated to allow free steam to enter the oil. The still was also provided with a small rectifying column, through which the vapors passed on their way to the condenser. When the still was filled, the steam was let on at first into the closed coils and then into the perforated coils also and the heating and steaming were continued until the distillate was brought to the proper fire test, which, in the case of the large stills above mentioned, would take about two days. Then the distillate had to be

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[1] See also U. S. Patent 845,735, Feb. 26, 1907.

cooled down preparatory for treatment with acid, the still was refilled, and its contents heated and steamed as before. During the steam-stilling the steam would carry over more or less of the burning oil, which would be recovered by the rectifying column and returned to the still. This procedure is objectionable as well because the prolonged subjection of the distillate to the temperature of the steam makes the color somewhat darker and the distillate harder to treat with acid and also because a great deal of time is lost and heat wasted.

By the method described by Frasch the low-test burning oil distillate is subjected to free steam, with or without being exposed at the same time to the dry heat of closed coils, and the resulting vapors are brought into repeated contact with a stream, more or less broken up and diffused, of preliminarily heated low test distillate mingled with hot water. This stream, constituting the supply of distillate to be raised in fire test, or at least a considerable part of the supply, is heated best by heat derived from the hot high test distillate from which the more volatile portions have been separated. The hot water with which the stream of distillate is mingled is water of condensation from nearly the whole of the injected steam. The water which returns along with the stream of distillate is separated by settling and decantation within the still or in an outside receptacle. By this process in order effectively to drive off the low boiling products, which may constitute twenty per cent, more or less, of the low test distillate, the latter need be kept at a steam heat only for a short time (under two hours—steaming for a few minutes, not over fifteen, having, it is said, given excellent results), so that the alteration in color can be reduced to a minimum, and, in fact, becomes hardly perceptible. Thus to shorten the time of steaming, the volume of distillate is limited relatively to the volume of steam admitted, but it follows from this concentration of the energy of the steam on so small a volume of distillate that the resulting vapors contain much more burning oil than those given off from the very much larger volume of distillate subjected to steam in the procedure indicated above. By bringing these vapors repeatedly into contact with the stream of preliminarily heated low test distillate mingled with hot water there takes place a fractional condensation which causes most of the burning oil to become condensed and united in this stream of distillate, while allowing the more volatile constituents (low boiling products) to pass away and, if necessary, the vapors can be subjected to further cooling, with the object of collecting any remaining portions fit for burning oil or of separating the vapors into various grades of naphtha.

The preliminary heating of the low test distillate is important in order that it may not condense the low boiling products. Practically a temperature of about 170° F. (77° C.) will be suitable for raising the distillate to 150° F. (66° C.) fire test and can be obtained by recovery of heat from the high test distillate hot from the steaming operation, but a less or even a greater degree of preliminary heating can be resorted to. The presence of the considerable volume of hot water is also important in equalizing the heat because of its high specific heat, and in modifying the condensing operation. The contact of the vapors with the stream of distillate not only has the effect of condensing a portion of the vapors (including the steam), but also of evaporating a portion of this distillate, so that the heat of the condensed vapors is utilized in aiding the distillation.

In subjecting the distillate to the free steam they may be brought together, in the same manner in which the low test distillate and the oil vapors are brought into contact with each other; but it is an advantage to admit the free steam into a traveling body of distillate at intervals in its line of travel. This body of distillate is supplied by a stream of distillate to be steamed at one end and discharging in a

stream of steamed distillate at the other Moreover, it is of further advantage to divide the traveling body into a succession of two, three, or more communicating pools and to make these pools diminish in depth, so that the removal of the last portions of the low boiling products takes place from a shallower layer than that (or those) from which the earlier portions are removed and that consequently there is less danger of retaining low boiling products in the distillate.

The apparatus as a whole consists, see Fig 30, of a distilling and rectifying column A, having a supply pipe A^1 opening into its upper part, a rectifying column B, discharging its products of condensation into the upper part of column A, a horizontal still C, which receives the liquids from column A and is provided with closed steam coils and perforated steam coils and also with a draw-off for the water, and a heat exchanger D connected with the outlet from still C by the pipe a, drainage-tank G, pump E, and pipe C, and with the upper part of the column A by pipe A^1. The heat exchanger is provided with an outlet d for the high test distillate
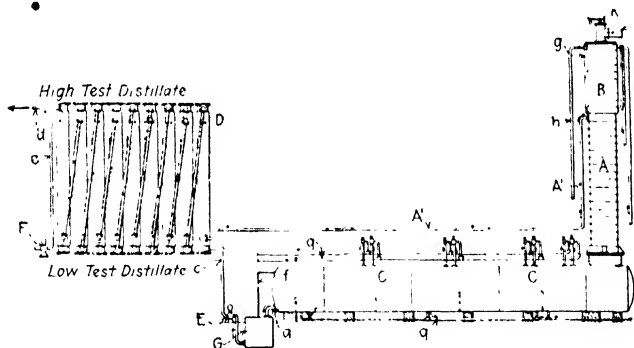
Fig 30 — Steam still, with heat exchanger and tower, according to Frasch

and an inlet e for the low test distillate whose fire test is to be raised in the column A and still C and which is preliminarily heated in the heat exchanger D by taking up the heat from the high test distillate, and so cooling the latter on its way through the heat exchanger The pumps E and F move the high test and the low test distillate, respectively, in opposite directions through the heat exchanger. The small pipe f is for equalizing the pressures in the still C and tank G.

The rectifying column B is provided with a water jacket g A special jacket, however, is not necessary to the rectifying action since it suffices to have the vapors repeatedly brought in contact with returning condensate from higher parts of the rectifying column

At h is an additional supply pipe entering the upper part of the rectifying column B for discharging distillate into it It can be usefully employed, for example, in filling the apparatus with high test distillate in starting, or it can be used to introduce low test distillate then or during the operation, the distillate in either case being preliminarily heated or not as the case may be The vapor outlet k from this rectifier B can be connected with an ordinary condenser (not shown)

The columns A and B are divided, as shown in Fig 31, into a number of chambers by horizontal partitions which are perforated and provided each with a pipe, bell and overflow pipes.

The still *C*, as shown in Figs. 30 and 31 holds liquid which travels horizontally through it, being supplied at one end by the stream from the column *A* through the lowermost pipes *m*, and discharging in a stream at the other through the pipe *a*, Fig. 30. At intervals are dams or partitions *o*, Fig. 31, to divide the traveling body of liquid into a succession of pools, which communicate by overflowing one into the other. This separation into pools aids in keeping the different parts of the body of liquid, which have been subjected to different degrees of steaming, better separated from one another. By making the dams or partitions *o*, Fig. 31, diminish in height toward the outlet *a*, Fig. 30, the horizontally traveling body of liquid diminishes in depth as it approaches the outlet *a*.
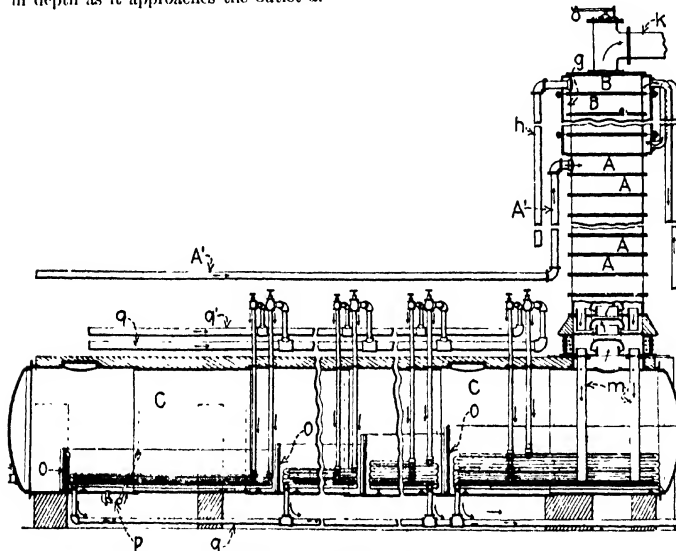
Fig. 31. — Steam still, according to Frasch, showing arrangement of "open" and "dry" steam coils.

The water which is delivered with the oil from the column *A* settles to the bottom of the still *C* and if not otherwise disposed of would fill the pools to the tops of the dams *o*. To allow it to pass from one pool to the next, each dam (except the last) is provided at the bottom with an opening. From the pool next the outlet *a* the water can be discharged by the draw-off *p*, Fig. 31, which is provided with a swinging arm that can be turned to raise or lower its open outer end, and so determine the depth at which the layer of water under the distillate shall stand.

In each compartment of the still *C*, except the small one drained by outlet *a*, are a closed steam coil and a perforated coil. The closed coil is supplied from the main with exhaust steam from engines used to supply power at the works, and discharges into the drain pipe *q* The perforated coil is supplied from the main q^1 with live steam.

The heat exchanger *D*, Fig. 30, consists of a number of connected elements, as many of these being used as may be judged useful to transfer heat from the

outgoing high test to the entering low test distillate, say ten. Each element resembles a tubular boiler or condenser in that it consists of a number of tubes between the partition plates of a shell. The shell is thus divided into two compartments or chambers by the partitions and the tubes, and the compartments are connected by the pipes into two series, so that the high test distillate starting at one end of one series may pass over one surface of the tubes (but inside, as shown), while the low test distillate starting at the other end of the other series passes over the other surface of the tubes (outside, as shown).

In raising the fire test of burning oil distillate with this apparatus the stream of low test distillate passes over the heat-conducting walls of the heat exchanger D in the opposite direction to the stream of high test distillate from the still C, so that in cooling the latter distillate the former is heated preliminarily to its introduction into the distilling and rectifying column A, say to 170° F. (77° C.), or more or less, according to circumstances, but most advantageously above the fire test to be secured in the distillate. The preliminarily heated distillate fed into the upper part of the column A descends through it and supplies the body of distillate in the still C. This being supplied at one end by a stream and discharging at the other end in a stream travels after the manner of a river and is subjected to free steam from the perforated coils at intervals in its travel, while at the same time it is heated by the dry heat of the closed coils. The vapors resulting from the action of the free steam (aided by the dry heat) pass up through the column A and are repeatedly brought in contact with the stream of preliminarily heated distillate until they pass into and through the rectifying column B, and so on to the condenser or condensers (not shown). As the vapors rise the chief part, or, in fact, nearly all of the steam from the perforated coils, is condensed, and mingling with the stream of preliminarily heated distillate forms part of the stream with which the later rising vapors are continually brought into contact. The oil condensed from the vapors also mingles with the stream, and as it descends is reevaporated more or less, so that there are repeated condensations and reevaporations, such that the oil-vapors from the still C are rectified and a naphtha suitably free from products fit for burning oil is obtained The rising vapors, which are acted upon by the incoming distillate (as also by the hot water and oil from condensations higher up in the columns) as a condensing agent, act in turn to vaporize some of the distillate, the vapors thus formed mingling with those from the still C and being rectified along with them Thus there is in column A both distillation — of the incoming preliminarily heated distillate — and rectification — of the vapors from the still C and from distillation of the incoming distillate in the column A. The vapors are subjected to a further rectification in the column B.

The body of oil in the still C is limited relatively to the volume of steam admitted through the perforated coils, so that all the low boiling products are removed in a short time. The rectification in the columns A, B serves to restore the products fit for burning oil which are evaporated at the same time by this rapid action of the free steam.

Assuming that the dams o, Fig. 31, are respectively twenty, twenty-four, twenty-eight, and thirty-two inches high and are located in a cylinder of five feet internal diameter at such places as to form compartments each nine and a half feet in length, it is recommended to use pipe for coils as follows, namely: in the first compartment, two hundred and thirty-eight feet of one inch wrought iron unperforated pipe for the closed coils and fifty-four feet of wrought iron perforated pipe for the open coils; in the second compartment, two hundred and four feet of one inch unperforated pipe and thirty-six feet of one inch perforated pipe; in the third

compartment, one hundred and fifty-three feet of one inch unperforated pipe and twenty-seven feet of one inch perforated pipe, and, in the last compartment, one hundred and nineteen feet of one inch unperforated pipe and eighteen feet of one inch perforated pipe. The perforations may be one-eighth-inch diameter, twelve inches between centers, and may be located on the under side of the pipes. The closed coils should be supplied with exhaust, the open coils with live steam. The supply of low test distillate is so regulated that enough to fill the oil spaces of column A and still C will be introduced by pipe A^1 every fifteen minutes. The supply of free steam is regulated to give oil of the desired fire test, and the temperature of the liquid in the jacket g is sufficiently below the boiling-point of water to prevent the passage of burning-oil hydrocarbons through the column B.

In raising its fire test about twenty per cent of the low test distillate may ordinarily be separated as low boiling products, but the percentage may vary. Thus if the composition of the low test distillate should vary, either from difference in the crude oil or in the process of distillation, the removal of a greater or a less percentage of naphtha might be necessary in order to have burning oil of the same fire test; but a variation may also result from a variation in the manufacturer's wishes with respect to the grade of burning oil to be obtained. For some grades a lower fire test suffices than for others, and the manufacturer frequently desires to retain in the burning oil the lowest boiling products which would be consistent with the desired fire test. The temperature of the liquid in the jacket g is adjusted to prevent these latter products from passing over with those whose presence in the burning oil would prevent it from having the desired fire test

The temperatures in columns A and B are such as to effect the condensation of the chief part of the steam let into the perforated coils of still C. The temperature in the still C is about that of water vapor under the barometric pressure inside the still -about 212° F. (100° C.) when the pressure in the still is not reduced below that of the outside atmosphere.

The horizontally-traveling body of oil in the still C being divided into a succession of communicating pools by the dams, the different parts are kept separate, and the dams being of diminishing height the pools are of diminishing depth, so that the free steam has less oil to pass up through - a condition which is believed to conduce to the efficiency of its action. In steaming the oil in the still C it is also an advantage to decrease the volume of free steam per cubic foot of oil as the latter approaches the outlet a, Fig. 30, because, the content of low-boiling products being less, it is not considered desirable to evaporate so large a proportion of the oil as in the earlier portion of the steaming operation, when the proportion of such products is greater.

As shown, the length of perforated steam coil is greatest in the pool next the column A and decreases in order, being least in the pool next the outlet a, and this decrease is in greater ratio than the decrease in the cubical contents of the pools, due to their diminishing depth toward the outlet. The volume of free steam decreases also, as shown, with reference to the square foot of exposed upper surface of the liquid being steamed.

Van Dyke and **Irish** describe a combination of still and condensers, which is used both for the distillation of gasoline and kerosene and also for lubricant and wax yielding oils. The design of the various parts is stated to result in a clean cut separation of the desired fractions. For example, contamination of water-white burning oils with more

highly colored hydrocarbons is said to be avoided. Condensation takes place entirely outside the still, i.e., the still is thoroughly and completely insulated. A special form of air-cooled reflux condenser is one of the features. This enables the rate of distillation to be as rapid as necessary but nevertheless is said to insure a good separation of the various fractions. Since the same still is used both for obtaining light oils and also for coking purposes, no loss due to transfer of residuum is occasioned.

Referring to some of the more recent methods for the distillation of petroleum in the form of undistilled residues containing all, or nearly all, the intermediate fraction in addition to the lubricant fraction of the petroleum, and also the distillation of undistilled residues resulting from a still further evaporation of the crude petroleum, but containing at least forty per cent of the lubricant fraction, Van Dyke and Irish[1] state that in current practice undistilled residues of the kind above first mentioned have been distilled partly with a view of increasing the yield of burning oil (kerosene) by cracking decomposable hydrocarbons of the lower boiling portion of these residues and partly with a view to obtaining distillate containing the undecomposed or only slightly decomposed hydrocarbons of the lubricant fraction of the crude oil; and the method adopted for reconciling these to a certain extent inconsistent objects has been to subject these residues to distillation first in stills with their tops exposed (fully or with slight protection only) to the atmosphere for cooling and thus partially condensing the vapors before they pass over to be condensed (the same still serving both for the preceding distillation of the crude oil or of a residue from it and for the cracking operation) and then the remaining portion is distilled in tar stills with their tops protected for keeping the vapors hot. The residuum from the cracking operation is transferred to the tar stills with intermediate cooling, settling and storage and in the case of petroleum obtained from the oil fields of Illinois and of other petroleum of analogous character also with subjection of the residual oil to treatment with sulphuric acid for separating coke and other heavy products of the cracking operation. The extent to which the cracking operation is carried has been regulated according to the judgment of the manufacturer in view of market and other conditions. The transferred residuum or tar has sometimes contained part only of the lubricant fraction of the crude oil and sometimes it has contained all the lubricants together with a considerable portion of the intermediate fraction.

The condensate which results from cooling the vapors in the exposed top stills has fallen directly into the liquid oil in distillation, or else has run down the still walls into the oil. The uncondensed portion of the so-cooled vapors has then passed over and been at once condensed (except very light products) by means of a water cooled condenser. The vapors from the tar stills, on the other hand, after passing over have been subjected to a series of two partial condensations in air cooled condensers before their complete condensation in a water cooled condenser, each partial condensation being effected in a single large pipe inclined upward and cooled merely by exposure to the atmosphere.

The following description by Van Dyke and Irish, involving the complete distillation of a crude oil, is given, since the heavier as well as the more volatile portions of petroleum may be considered to be potential sources of gasoline.

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[1] (J. S. C. I. 1913, 972; U. S. Patent 1,073,548, Sept. 16, 1913.)

At the end of a run, before opening the stills for cleaning out, it has been the practice to fill with free steam, in order to expel the hydrocarbon vapors; and these with the steam have been passed through the condensers employed in the distillations. When the residual petroleum has been withdrawn from the exposed top stills much matter has been left adherent to the interior of the stills; and there has thus been a direct loss (because the adherent matter is in part, of value) and also an indirect loss because time and labor are required to clean out the still after each run preparatory to the next.

The necessary cooling of the residual oil and its storage also involve a loss of time and labor; and there is a further loss of valuable material in the matter which settles out in the storage tanks or is removed by the additional special treatment needed with petroleum of the kinds obtained from the oil fields of Illinois, Kansas, Oklahoma and Texas.   Van Dyke and Irish observe that whenever the distillation in the exposed top stills has been carried farther than or not so far as the point at which no more and no less residuum is made than the tar stills have capacity to distill, a part either of the exposed top stills or of the tar stills of the plant must be idle. Further, from various causes, the separation of hydrocarbons in the partial condensations has been, it is said, very imperfect.   One cause is the lack of control over the cooling effect produced on the vapors.   Different installations have differed in the area and degree of exposure of the air cooled (condensing) walls, according to the views of the manufacturer; but with any given installation the cooling effect produced on the vapors has been, it is noted, customarily controlled solely through regulation of the still fires.   By slackening these, the rate of evaporation in the still can be lessened; and less heat being then imparted by the vapors to the heat conducting walls, these fall in temperature and condense a larger proportion of the passing vapors (although the absolute volume condensed is smaller than before). By urging the fires, evaporation is increased; and the heat conducting walls rise in temperature and condense a smaller proportion (but more absolutely) of the evolved vapors.   There are, however, variable conditions in a run or in different runs, due to the varying temperature of the air or other meteorological conditions and to variations in the oil in distillation in a run or to be distilled in different runs, which cannot be met as completely as would be desirable by regulation of still fires; and, besides, it is not possible to insure a perfect regulation of them at all times.   The cooling of the vapors, it is added, has not been thorough; nor has proper opportunity been afforded for interchange of hydrocarbons between the condensate and the vapors.

Various proposals have been made for improving the separation of petroleum hydrocarbons by partial condensation of their mixed vapors; but in spite of them, it is maintained, the current practice has been as stated.   Because of the imperfect separation different cuts of distillate have contained hydrocarbons which, if not positively objectionable, could be more advantageously utilized as constituents of other cuts.   For example, hydrocarbons which are sufficiently colorless and are otherwise suited for water white burning oil (kerosene) distillate are made (as a result of imperfect separation) to pass into distillate of poorer quality; because they are accompanied by hydrocarbons too highly colored or otherwise unsuited for water white oil.   In like manner the yield of lubricant stock (or of lubricant stock and wax yielding material) is diminished by imperfect separation; because this results in the first of the desired hydrocarbons being accompanied by hydrocarbons which are undesirable in such stock.

By using a method devised by these investigators it is said that those products, for the obtainment of which the current practice was adopted, can be obtained without the loss of time, labor and material incident to the customary transfer of residuum and also without the loss in enforced idleness of part of the plant which results whenever the tar stills are of insufficient capacity for distilling all the residuum of the desired character which can be made in the exposed top stills, or conversely are able to distill more of such residuum than the latter stills can furnish. The products mentioned can be obtained, it is said, of better quality or in larger amount. If it should be preferred to obtain distillate with a smaller yield of cracked products, it is possible to do so without necessarily carrying over into the distillate more than a small proportion of the lubricant (or lubricant and wax yielding) hydrocarbons.

By the improved method crude petroleum is distilled, until the required residue is obtained; and this residue is then subjected to distillation at the requisite high temperatures uninterruptedly in two stages; the earlier of which is conducted with a view to condensing out of the mixed mass of vapors for return to the oil in distillation, those hydrocarbons which it is desired to have in the lubricant stock (or the lubricant stock and wax yielding material) and also those hydrocarbons which it is desired to crack into lighter oil, while allowing the other hydrocarbons to pass over to be condensed as distillate and distillation is terminated while the residual oil represents a large part (not less than 25 per cent) of the lubricant fraction of the crude oil. The next stage of distillation is then begun and is conducted with a view to obtaining mainly undecomposed hydrocarbons of this fraction, a suitable temperature difference (say of about 100° F. to 150° F. (56° to 83° C.) or more) for holding back the desired lubricant, hydrocarbons being maintained in the earlier stage between the liquid oil in distillation and the vapors passing over to be condensed as distillate, and a less temperature difference maintained in the later stage between them — say a difference which is smaller than that of the earlier stage by 50°-75° F. (28°-42° C.). Distillation, in the earlier and in the later stages, is performed under atmospheric pressure, or nearly so, and without the injection of steam into the stills. During the later stages the vapors in the still should be protected against conductive cooling to the extent at least to which they would be subjected in an exposed top still; because such cooling would needlessly increase the fuel consumption and would involve a wasteful decomposition of hydrocarbons; and in the earlier stage it is advantageous to protect the vapors in the still against conductive cooling and to subject them after
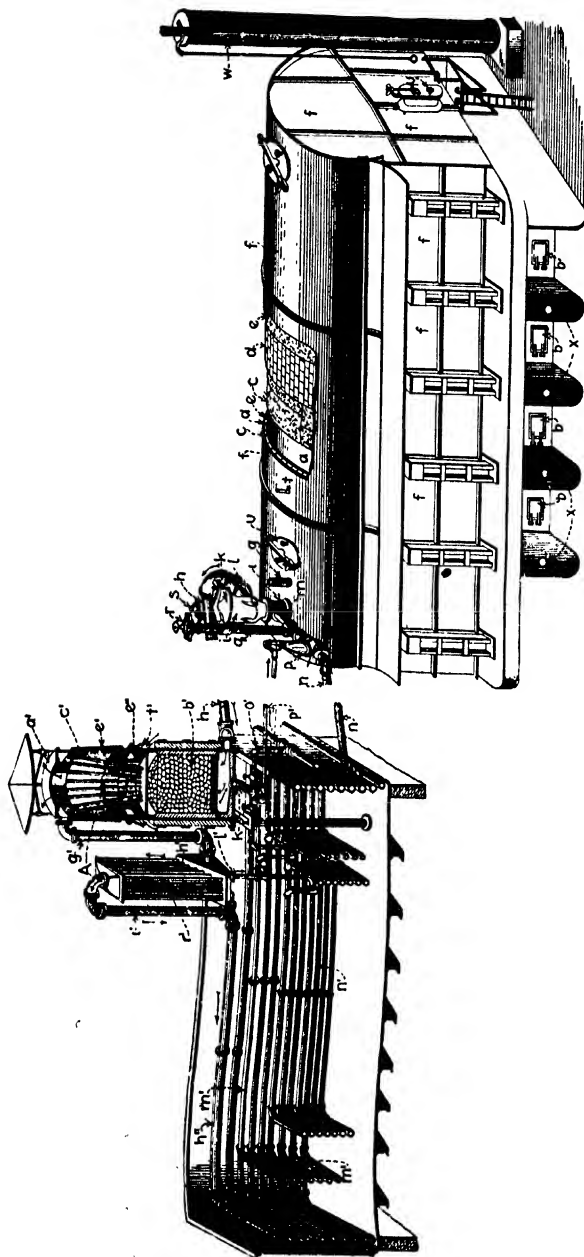
Fig. 32. — Fire still, according to Van Dyke and Irish.

they leave the still to cooling necessary to form sufficient condensate for return to the oil in the still for reëvaporation; because a cleaner separation of hydrocarbons can be effected outside of the still than in it.

The still a, Fig. 32, is shown in the form of a horizontal cylinder heated by a number of fireplaces whose ash pit doors show at b. It is protected against loss of heat by blocks c, brick-work d and cement e; and it is covered with sheet metal f. There is a pipe g for filling the still with oil and a pipe h for conducting away the vapors. This vapor pipe is connected with the vapor space of the still a by means of a short upright pipe i having a removable cover k. A side opening receives the end of the vapor pipe h. Below this side opening is a flap valve whose operating handle is seen at l; and below that valve is another side opening which receives the pipe m, a continuation of which is formed by pipe n having a valve p. In running, the flap valve is open and the valve p closed. At the end of a run, when steam is introduced into the still to expel the vapors, their positions are reversed.

The pipe q, which joins the pipe m, is provided with a safety valve r and a vacuum valve s. A pipe t is provided for introducing steam into the still at the end of a run before opening the manholes u for cleaning out. At w is the chimney for the fires under the still. At x are holes for pipes to deliver still gases or other fuel gases under the still for burning.

The vapor pipe q leads to a condenser in the form of numerous pipes A, Fig. 32, arranged in parallel between header a' and chamber b'. In Fig. 32 the vapor outlet ends of these pipes are at a higher level than their vapor inlet ends; so that the condensate, which is formed in each pipe and naturally runs downward, will flow oppositely to the corresponding stream of vapors. In order to equalize the flow of the vapors among these pipes, the aggregate cross section of the passages at their narrowest points is proportioned with reference to the passage of a definite volume of vapors per unit of time under a given pressure; and, in order that the streams may be longer exposed to cooling in pipes of given length, their average cross sections are made greater than those at the narrowest points and the outlet ends of the pipe are strictured. These strictured outlets constitute the narrowest points. The pressure in these pipes is automatically released should it become excessive at any time. The best arrangement is that in which the strictured outlet is formed in the body of a light valve which rests by its own weight over the end of the pipe.

Fig. 33. — Detail of vapor outlet valve on air-cooled condensing tubes of Van Dyke and Irish still.

While dimensions and proportions can be varied, good results have been attained, it is said, for a still holding a thousand barrels of oil up to the usual level, with an air cooled condenser having fifty-six of the pipes A, Fig. 32, each eleven feet in length and four inches in external diameter (giving about 665 square feet of cooling surface on the heat conducting walls of pipes A). A circular vapor outlet opening c' of an inch and a quarter diameter would suffice for each pipe A, the vapor pipe h having an internal diameter of twelve inches and the valves d', Fig. 33, weighing about thirty-three ounces each.

The pipes A are cooled by controllable currents of air. The header a' is annular and forms part of a passage for the air currents in the middle of the group of pipes A; while the top of the chamber b' is a circular disk and obstructs passage at its bottom; and the pipes A are enclosed in a casing e', Fig. 32, which fits around the header a' at the top and has inlet openings e'' (Fig. 32) at the bottom for inflow of air from the surrounding atmosphere. Each inlet is provided with a valve which can be opened wholly or in part, or can be completely closed. Air currents are produced in the casing by heat absorbed from the walls of pipes A. The vapor pipe h leads from the still directly to the chamber b', Fig. 32. This chamber is much deeper than a mere manifold or header (the depth represented being about three-fourths the length of pipes A). It is provided with a non-conducting jacket. In it, resting on a grate, are pieces of cobble stones of four to eight inches in diameter. The condensate from pipes A flows down over the stones and is given by them a back and forth transverse motion; while the vapors which rise upward between them are similarly deflected; and the vapors then pass into the pipes A for cooling conductively in streams of small diameter.

The vapor outlet of the air cooled partial condenser A a' b' is connected by pipe g' with the vapor inlet of a second partial condenser h' composed of numerous pipes set between headers and exposed to the air for cooling. The vapor outlet from condenser h' is connected by pipe i' with a water cooled condenser, which is a coil placed in a water tank which is supported on walls and cross beams.

Thus the vapors from the still (a) flow successively through two partial condensers, each of them cooled by air and then through a water cooled condenser.

The liquid outlets k' (Fig. 32) and l' (Fig. 32) of the partial condensers are respectively connected through U traps with the water cooled draw off pipes m' and n' placed in water tank. The water cooled draw off m' is valved and is connected with outlet k' by means of a cross which also serves to connect this outlet with two other valved pipes o' and p' respectively, pipe o' being a draw off for condensate from the chamber b' when the condensate becomes too thick to flow at the temperature of the cooling water in the tank and pipe p' being a "run back" leading to the still a. The pipe o' is maintained at a higher temperature than the draw off m'. It may have such higher temperature merely because exposed to the air instead of being immersed in water; or it may be heated.

The vapors generated in still a pass by pipe h to chamber b' and on reaching the top of this chamber they are divided into numerous streams, one for each of the pipes A. These streams flow in parallel inside the heat conducting walls of the pipes and are surrounded by air for cooling and are further equalized among themselves by the stricturing which they are given at their outlets by passage through the restricted openings c'. Should the pressure become excessive, one or more of the valves d', Fig. 33, rise and automatically release the pressure, the released vapors passing on to condenser h'. The vapors flow in opposite directions in pipes A to the corresponding streams of condensate formed by the cooling in them; and a good opportunity for exchange of hydrocarbons is thus afforded, more volatile hydrocarbons in the condensate replacing less volatile in the vapors.

The flow of the air past the pipes A tends to uniform and efficient cooling of the vapors. The vapors are brought into intimate contact in chamber b' with the condensate for interchange of hydrocarbons,

while they are protected against indirect cooling. For a continuous complete distillation of crude petroleum in the still *a*, the latter is filled with the proper charge of crude oil (say, a thousand barrels) and is heated; the heating is continued until the still contents become dry or nearly so, wax tailings coming over as the last distillate.

During the first part of the run the portion of the crude oil which is more volatile than the intermediate fraction mentioned above, is received as distillate; while during the remainder of the run, which is conducted in two stages, the intermediate and the lubricant (or lubricant and wax yielding) fractions are distilled, the former with more and the latter with less decomposition (cracking) of constituent hydrocarbons. The later of these stages is advantageously commenced as soon as or shortly after a percentage of the crude oil equal to the more volatile portion plus the intermediate fraction has been received as distillate. During the first part of the run and the earlier of the two stages referred to, the run back is open and the draw offs are closed. During the later stage, the run back *p'* is closed and the draw offs *m'* and *o'* are opened one at a time, the former as long as the distillate from bottom of chamber *b'* is thin enough to flow at the temperature in pipe *m'*, and the latter subsequently. The temperature difference between the liquid oil in distillation and the vapors which have passed over to be condensed as distillate is greater in the previous distillation than in the later stage. In the former, the vapors are made to flow through the partial condenser *A a' b'* before they pass over to be condensed as distillate, all such condensation being performed in the air cooled partial condenser *h'* and in the water cooled complete condenser and the condensate from condenser *A a' b'* returning by run back *p* to the oil in distillation in still *a*; while in the later stage they are condensed as distillate as soon as they have passed out of the still *a*. Until then they are protected against conductive cooling by the nonconducting jacket *c, d, e* on the still; so that the temperature difference between the liquid oil and the vapors passing over is correspondingly small.

The total flow of distillate at any time can largely be controlled by regulating the fires; but with equal evaporation per hour the collection of distillate per hour will naturally be larger when it includes condensate from condenser *A a' b'* than when it does not. It is advantageous so to regulate the still fires that the total flow per hour of distillate diminishes during the distillation of part at least of the intermediate fraction, as compared with the average of such flow during the distillation of the more volatile portion of the crude oil, and that the combined flow per hour from the condensers *h'* and *h''* (exclusive of condenser *A, a', b'*) during the distillation of part at least of the lubricant fraction should equal or exceed the average of the flow during the distillation of the intermediate fraction; while the average flow of distillate per hour at the same time from the condenser *A, a', b',* may well itself exceed the same average. The flow of distillate from each condenser varies from time to time according to the nature of the oil; and the flow from condenser *h''* may cease before the beginning of distillation of the intermediate fraction. If so, it should be flowing again before the close of such distillation.

During the distillation of the intermediate fraction and also of the lubricant fraction the vapors are cooled in condenser *A, a', b',* to temperatures between 400° F. and 600° F. (204°–316° C.) so that the uncondensed portion of these vapors may be as free as practical from lubricant and wax yielding hydrocarbons. Any desired cuts in any distillate can be made by directing the stream to different distillate receivers.

The air inlet valves r' would be more nearly closed at the beginning of each run, when light hydrocarbons are being distilled, and also at the end of each run when the volume of vapors is comparatively small, than they would be during the intermediate part of the run. In other words, the currents of air are controlled to increase and decrease in a general way the cooling effect on the vapors according to the varying volume and temperature of the latter. These air inlet valves would also be closed more when the weather is cold or windy and less (if at all) when it is warm or still. The valves r' can also be manipulated to counteract or to compensate for other variables. In general, observation of the streams from the respective condenser outlets, with test of samples, should give sufficient indications.

At the end of the run the valve p in pipe n is opened and the valve l is turned to close the ordinary vapor pipe h. Steam is then introduced through the pipe t. It fills the still a and expels the hydrocarbon vapors. They pass, with steam, through the pipes mn to any desired place or receptacle without entering the condenser A, a', b', the condenser h' or the condenser h''; so that at the next run the first runnings of condensate are not composed in part of hydrocarbons expelled by the steam. So far as concerns the condensate from condenser A, a', b', as this returns to still a, the presence in it of hydrocarbons would be of small importance; and it is, therefore, of minor importance for the valve l and valved branch pipe n to be between condenser A, a', b' and the still a. After expulsion of hydrocarbon vapors, the steam is shut off; and the still a is allowed to cool, is opened, cleaned, closed and then receives a new charge of petroleum.

In a complete distillation of one thousand and forty-six barrels of crude petroleum having a gravity of 33.6° Bé. and yielding paraffin wax the following figures have been observed.

Time after bringing in the still

Distillation of portion more volatile than the intermediate fraction, as shown by the liquid oil in still a attaining 600° F. .... 19¼ hrs.

Distillation of intermediate fraction, as shown by liquid oil in still a being above 600° F. and the condensate from condenser A, a', b', having a viscosity less than 65 seconds at 100° F. by Saybolt's universal viscosimeter .. .. 18 hrs.

Distillation of lubricant and wax yielding fraction, being residue after removal of intermediate fraction and lighter portion .... 17 hrs.

Total .... 54¼ hrs.

Flow of distillate

Distillation of portion more volatile than intermediate fraction:
Condenser h'', 147 barrels; condenser h', 211 barrels. .... 358 bbls.
Average per hour both condensers...................... 18.5 bbls.

Distillation of intermediate fraction:
Condenser h'', 15 barrels; condenser h', 203 barrels........ 218 bbls.
Average per hour both condensers...................... 12.1 bbls.

Distillation of lubricant and wax yielding fraction:
Condenser h'', 64 barrels; condenser h', 113 barrels; condenser A, a', b', 257 barrels................................ 434 bbls.
Average per hour first two condensers. .... 11.1 bbls.
Average per hour all three condensers.................... 27.1 bbls.

Average per hour of first half of distillation from first two
   condensers.. 17.3 bbls.
Average per hour of first half of distillation from all three
   condensers.. 37.1 bbls

Gravities of distillates

Distillation of portion more volatile than intermediate fraction:
   Condenser h'':
      Lightest .... 70.7° Bé.
      Heaviest .... 48.8° Bé.
   Condenser h':
      Lightest............. ... . 63.5° Bé.
      Heaviest .... 40.5° Bé.
Distillation of intermediate fraction:
   Condenser h'':
      Lightest.... .. .. 57° Bé.
      Heaviest............... .... 47° Bé.
   Condenser h':
      Lightest.... .. .. 40.5° Bé.
      Heaviest............ .... 34.8° Bé.
Distillation of lubricant and wax yielding fraction:
   Condenser h'':
      Lightest .... 55.7° Bé.
      Heaviest .... 41° Bé.
   Condenser h':
      Lightest.... .... 37.6° Bé.
      Heaviest........ .... 28° Bé.
   Condenser A, a', b':
      Lightest ... . 31° Bé.
      Heaviest received by water cooled pipe m' .... '11° Bé.

Temperatures after bringing in still

Distillation of portion more volatile than intermediate fraction:
   Oil in still a:
      Lowest............. ... . 210° F.
      Highest........... . . .. 600° F.
   Vapors passing over to be condensed as distillate (in header
     a'):
      Lowest .... 168° F.
      Highest........ .. . . 480° F.
   Temperature difference, average .... 97 5/10° F.
   Vapors leaving still a (in pipe i):
      Lowest.. 193° F.
      Highest....................................... 560° F.
Distillation of intermediate fraction:
   Oil in still a:
      Lowest....................................... 600° F.
      Highest....................................... 700° F.

Vapors passing over to be condensed as distillate (in header a'):

Lowest.. 470° F.

Highest... 570° F.

Temperature difference, average......................... 151° F.

Vapors leaving still a (in pipe i):

Lowest.. 560° F.

Highest... 660° F.

Distillation of lubricant and wax yielding fraction:

Oil in still a:

Lowest.. 691° F.

Highest........ .... (See note).

Vapors passing over to be condensed as distillate (in pipe i):

Lowest...... .... 644° F.

Highest............................ .... 810° F.

Temperature difference, average.......... ... . (See note).

Vapors after first fractional condensation as distillate (vapors in header a'):

Lowest.. 317° F.

Highest... 607° F.

NOTE. — By an accident the temperatures in the liquid space of still a were not observed at the last seven periods of hourly observation. From other experience it is estimated that the highest temperature in the liquid space in the still was about 850° F.; and (using so estimated temperatures for seven of the eighteen intended observations) the average temperature difference during the distillation of the lubricant and wax yielding fraction is estimated to have been 46° F. The average temperature difference at the eleven actual observations was 50° F.

The heating of the still was continued for three hours after the distillate ceased to flow from condensers h' and h'' and for two hours after that from condenser A, a', b' was turned into pipe o' (wax tailings). In the last hour of flow from condenser A, a', b', through pipe m' only one barrel of distillate (gravity 11° Bé., at 60° F.) was received. In the hour previous half a barrel (gravity 55.7° Bé.) was received from condenser h'', one barrel (gravity 35° Bé.) from condenser h', and two barrels (gravity 18.5° Bé.) from condenser A, a', b'.

Distillate did not flow from the condenser h'' in the distillation of the intermediate fraction during ten hours, and in the previous distillation during four hours. Distillate commenced to flow first from condenser h'' and was running two hours and twenty minutes before it commenced to flow from the draw off n' of condenser h'. These hours of no flow in one or other condenser are considered in estimating the average flow as given in table. More than half the distillate in the distillation of the lubricant and wax yielding fraction was received in the first six hours; and the flow during such six hours is the basis for the average flow per hour of first half of distillation of this fraction. Twelve thousand two hundred pounds of coke were removed from the still at the end of the run.

In practical working it is unnecessary to ascertain temperatures; since observation of the distillates and returning condensate will give sufficient information to an experienced stillman.

If it is necessary, the earlier stage of the distillation of the undistilled residue composed of the intermediate and the lubricant and wax yielding fractions of the crude oil can be prolonged into the distillation of the latter fraction, this stage

being terminated while the desired portion, not less than twenty-five per cent, of that fraction remains in the still.

Should it not be feasible to conduct the complete distillation of the crude oil in the still *a*, all, or any part, of the portion more volatile than the intermediate fraction can be distilled off in another still. The residual oil can then be subjected to uninterrupted distillation in the still *a* in two stages; and, if preferred for any reason, the distillation can be carried further before transfer to the still *a*, provided the residual oil to be subjected to distillation uninterruptedly in those two stages containing at least forty per cent of the lubricant and wax yielding fraction of the crude oil.

The lubricant fraction and the intermediate fraction taken together of any given crude petroleum are defined as the percentage by volume of the crude petroleum which remains in the still when the still's contents attain a temperature of 600° F. (or the temperature commencement of cracking in case it should be lower than 600° F.) in a distillation of the crude petroleum in the ordinary way under atmospheric pressure without introduction of steam into the still; and the lubricant (or lubricant and wax yielding) fraction is represented by the percentage by volume of the crude petroleum which remains in the still when portions of distillate from the outlet of the customary water cooled condenser first exhibit either a viscosity as high as 65 seconds at 100° F. by Saybolt's universal viscosimeter or a cloud at a temperature as high as 50° F. (whichever characteristic is first exhibited) in a distillation of the crude petroleum with introduction of free steam in suitable volume to prevent cracking. For concordant results the distillations (or assays) must always be performed in the same manner.

In distillation under atmospheric pressure without introduction of steam into the still, the heat may be so regulated that distillate is received from the condenser at the uniform rate of about eight per cent by volume per hour of the charge of crude oil. The distillates may be received in two per cent portions; and they should be tested for flashing points by the closed cup method, after removal of hydrogen sulphide, when this is present. The temperature of the oil in the still at the completion of each portion should be noted. When the flashing points begin to exhibit a progressive recession, it will be known that cracking has set in, and the temperature at the completion of the portion of maximum flashing point may be taken to be the commencement of cracking. Should this temperature be below 600° F., the percentage of the crude oil then remaining in the still represents the intermediate and lubricant (or lubricant and wax yielding) fractions of the crude oil (taken together), the percentage previously collected as distillate representing the more volatile portion of the same crude oil. If this temperature of commencement of cracking be above 600° F., the percentages when the liquid oil attains 600° F. are to be taken.

In the distillation with introduction of free steam into the crude oil the heat may be so regulated that hydrocarbon distillate is received from the condenser at the uniform rate of about fifteen per cent by

volume per hour of the charge of crude oil; and the free steam supply is so regulated that the stream from the condenser contains water of condensation equal in volume to from a third to a half of the hydro-carbon distillate. The steam may be dry and saturated; or it may be slightly superheated. The distillates may be received in two per cent
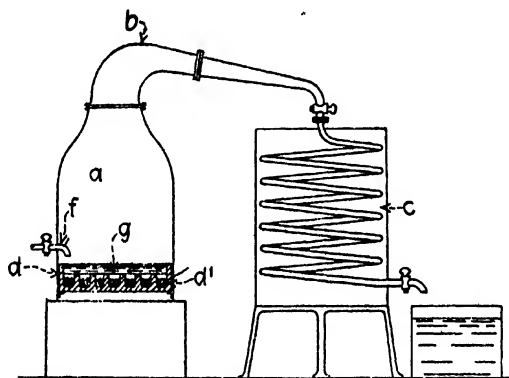
Fig. 34. — Electrically heated still, according to McClelland.

samples; and they should be tested for viscosity and (when the petro-leum yields paraffin wax) for cloud (paraffin wax content) also. When a portion exhibits either a viscosity as high as 65 seconds at 100° F. by Saybolt's universal viscosimeter or a cloud at a temperature as high as 50° F. (whichever characteristic first appears) the undistilled residue
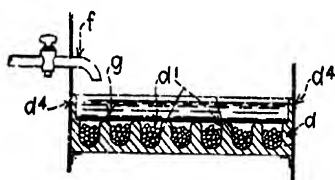
Fig. 35.

represents with sufficient accuracy the lubricant (or lubricant and wax yielding) fraction of the petroleum. The difference between it and the percentage representing the inter-mediate and lubricant fractions taken together represents the inter-mediate fraction of the crude petroleum. The portions of dis-tillate to be tested for viscosity (or viscosity and cloud) should be separated by settling and decantation from the accompanying water before they are so tested.

T. McClelland [1] proposes to distill liquids and solids, including petroleum, by direct contact between the substance being distilled and electrically heated resistance material, for example, carbon. In

[1] British Patent 15,263, June 25, 1910.

Fig. 34 the still a has in its lower portion a receptacle d, made of porcelain. As shown more in detail in Figs. 35 and 36, this receptacle has deep grooves or channels d^1 which form a continuous path due to openings or communications d^2 at the ends. These grooves are filled with granules of carbon. Carbon connecting pieces e^1 are connected to a source of electric current. By covering the carbon with oil, or by spraying oil onto the carbon, which is heated by the passage of an electric current, heat is directly transmitted to the substance being distilled.
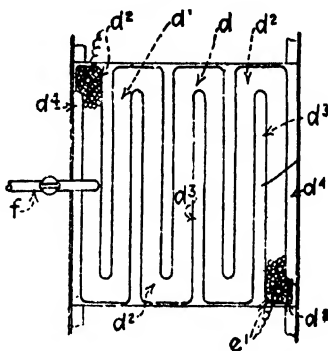
Fig. 36.

Gathmann [1] distills oils in a partial vacuum in the presence of a gas which is circulated through the oil in the still and condenser and is used over and over again. The gas which is circulated may be air or a noncombustible gas such as nitrogen or carbon dioxide.

J. H. Parker [2] separates petroleum into its fractions by means of a series of pairs of retorts, each pair vertically disposed above and connected with the next underlying pair. The individuals constituting each pair of retorts are located in the same horizontal plane. There are eight pairs of retorts and each pair is provided with an individual exhaust pump, pressure tank and condenser. The battery of retorts is inclosed in a furnace setting. The lower four pairs are heated by direct heat; but each pair is heated to a different and successively lower temperature than the next lower pair by means of interposed diaphragms. The four upper pairs are steam jacketed.

Each retort really constitutes a small still in itself. Distillation takes place under pressure. In the case of the four upper pairs, vapors escape from one retort in a pair to the other retort in the same pair, are there subjected to contact with purifying material and are then removed and condensed. Material which does not vaporize forces itself into the corresponding retort in the next lower pair and is here subjected to a somewhat higher temperature and so on. The oil is thoroughly atomized in each retort by means of steam and mechanical atomizers.

The process aims to effect a rapid separation of petroleum into its fractions and to produce fractions, the components of which have distinctive characteristics, and which possess properties sharply differentiated from the properties of other fractions.

[1] U. S. Patent 768,796, Aug. 30, 1904.
[2] J. S. C. I. 1910, 807; U. S. Patent 958,820, May 24, 1910.

For special dephlegmating devices for separating petroleum vapors by fractional condensation see **C. R. Ewing,**[1] **W. C. Koehler** and **L. Link.**[2] **G. H. Gillons**[3] also shows a special device for fractionating oil vapors.

W. Landes[4] is of the opinion that much of the gasoline now on the market contains heavy components which become separated from the lighter and more volatile hydrocarbons and settle at the bottom of the automobile or other fuel tanks. These heavier constituents, containing a larger percentage of carbon than the lighter and more volatile bodies and being the first to be drawn off and used, are said to carbonize the working parts of the motor and destroy the efficiency of the more
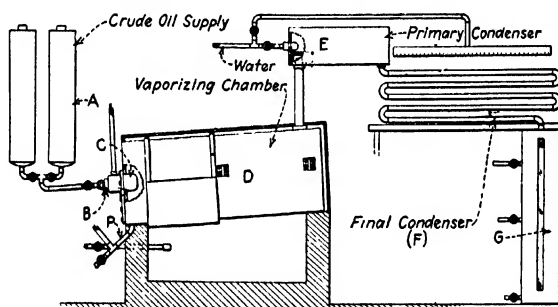
Fig. 37. — Vaporizing apparatus proposed by Landes.

highly volatile hydrocarbons which (assuming that the above separation does take place) are the last to be used.

With this in view Landes has devised a method for producing a highly volatile motor fuel from crude petroleum which consists in placing the crude petroleum in a tank, or a number of tanks A (Fig. 37), and subjecting the crude petroleum to high pressure, to force it through an exceedingly fine atomizer or spray nozzle B (Fig. 37). The latter is supported in a steam casing C which is located within and at one end of an elongated chamber D previously heated to a temperature of approximately 180° F. (82° C.).

The crude petroleum under pressure while within the nozzle is first heated and expanded by the steam within the steam casing which surrounds the nozzle, and is additionally treated with the steam, directed

[1] U. S. Patent 1,083,998, Jan. 13, 1914.

[2] U. S. Patent 1,084,016, Jan. 13, 1914.

[3] U. S. Patent 1,084,080, Jan. 13, 1914.

[4] J. S. C. I. 1916, 1211; Chem. Abs. 1916, 3157; U. S. Patent 1,199,909, Oct. 3, 1916.

transversely to its path, as the petroleum issues from the nozzle through the restricted orifice in it and previously to its entering the heated chamber. Thus the crude petroleum is injected into the heated chamber D in an exceedingly fine spray, whereby the lighter and more highly volatile components, such as cymogene, rhigolene, petroleum ether, and the more volatile constituents of the gasoline, are instantaneously liberated and vaporized. The mist of steam and oil vapors travels the entire length of the heating chamber D, before passing to the primary condenser E. This gives the volatile components plenty of time to vaporize and also allows heavier hydrocarbons to condense.

The atomizer, shown in detail in Fig. 38, consists of the pipe nozzle a, having one of its ends connected to the body of the valve b of the oil
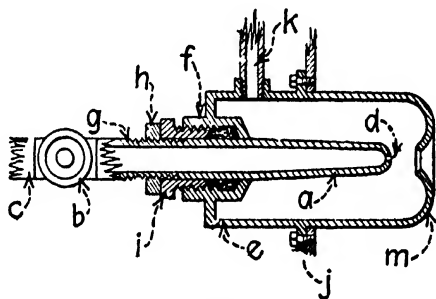
Fig. 38

pipe c, and having its opposite end closed, with the exception of the minute opening or aperture d through which the crude petroleum under pressure is discharged in an exceedingly fine stream. The nozzle a projects into the steam casing or steam chamber e through the packing box f provided in one of its ends, and for adjusting the position of the nozzle a within the steam casing e, the nozzle a is provided with the threaded portion g, upon which is screw threaded the adjusting nut h which bears against the gland i of the packing box f of the steam casing. The steam casing e is provided with the central annular flange j, for securing the steam casing upon the forward end of the retort or heated chamber D (Fig. 37). The portion of the steam casing at the outer side of the heated chamber D is connected by the steam pipe K to any source of steam supply under pressure of approximately seventy-five pounds. The end of the steam casing e which projects through the front end of the chamber D is closed by the inwardly curved end wall m which is provided with a central restricted aperture registering with the aperture of the oil pipe nozzle a, the space or distance between the

aperture of the nozzle a and the aperture of the end wall m of the steam casing being regulated by the adjustment of the oil nozzle by means of the adjusting nut h.

By the employment of the specially constructed atomizer above described, the crude petroleum under pressure and expansion is forced through the aperture of the nozzle a in an exceedingly minute stream, which is cut transversely by the steam which flows through the steam casing toward the end of the atomizer which projects into the Heated chamber D.

The steam is caused to thus cut transversely across the stream of oil by being deflected by the inwardly curved end m of the steam casing. This action upon the minute stream of oil again expands it and causes the particles of the oil to become so thoroughly dissipated that the oil issues from the atomizer in a fine mist, whereby the particles of the crude' petroleum further expand and instantaneously burst into vapor or gas upon coming into contact with the previously heated air within the chamber D. The mist causes the liberation of the highly combustible and volatile components of the crude petroleum, and separation of the heavier and less volatile components of the oil. This liberation and separation continues during the passage of the vapor or gas through the heated air within the elongated heated chamber D toward the opposite upper end portion of the chamber.

The heavier and less volatile components descend upon the inclined bottom of the heated chamber and are removed through the draw-off pipe P (Fig. 37).

From D (Fig. 37) the mist of light oil vapors and steam passes to the primary condenser E, where they meet a direct spray of cold water. The mixture of water and partly condensed vapors then passes to final condensing coils F and receiver G.

C. H. Boorman [1] has designed an organization of column stills, dephlegmators, heat exchangers and separators which are intended to distill petroleum continuously with the heat derived from superheated steam. Only a small portion of the steam used is allowed to condense. Most of it remains in the form of a gas, is recirculated through a super- heater and used over and over again. Light benzine, illuminating oil and heavy residue are continuously produced, the benzine in one column and the illuminating oil and residue in a second column. Apparently the process is primarily designed for continuous, straight distillation, without cracking. The stills used are essentially vertical dephleg- mating columns.

[1] J. S. C. I. 1917, 498; U. S. Patent 1,220,067, March 20, 1917.

R. C. Dundas [1] sprays oil into the bottom of a vaporizing chamber and heated gases are supplied to the upper outer portion and led down around an annular baffle or flue to the lower portion of the chamber where they mix with the sprayed oil. The gases and oil spray and vapor are then passed up through the inside of the annular baffle or flue. Fig. 39 shows an arrangement of four towers for continuous distillation. Oil is sprayed into the bottom of tower D, is partly distilled, the residue is pumped to tower C and so on. Distillation is effected by means of hot gases which come from the flue K and pass through the towers in the direction shown by the arrows. Condensates of varying gravities collect on the troughs. The final residue is pumped
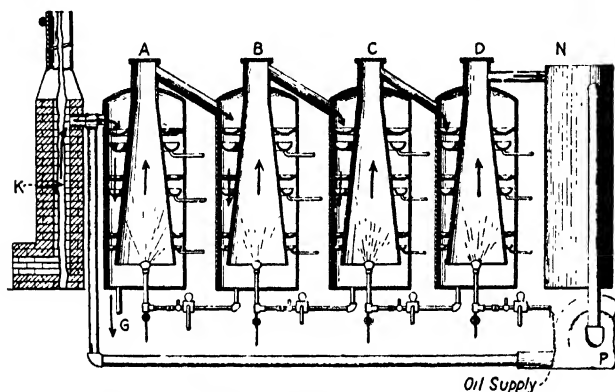
Fig. 39. — Distilling method proposed by Dundas.

out at G. There is also an arrangement as indicated at P for recirculating the gases.

Corthesy and **Castelli** [2] describe a continuous method of fractionating crude petroleum in which the oil flows downwardly and is exposed to consecutively increasing temperatures in its downward flow. Oil is fed into the top of a cylindrical still through a number of perforations; the unvolatilized portion is discharged at the bottom and the vapors pass out through a pipe at the top to a condenser. A portion of the vapor is drawn off from the outlet pipe by means of a suction fan, and after passing through a superheater within the furnace, is led into an annular space around the still and then into the still through a series of tangential slits, whereby a whirling or vortex action is produced within the chamber and unvolatilized particles are thrown by centrifugal force towards the walls.

[1] Chem. Abs. 1918, 993; U. S. Patent 1,257,199, Feb. 19, 1918.
[2] J. S. C. I. 1919, 526 A; British Patent 127,690, May 1, 1918.

H. D. Lorch[1] claims to fractionate the vapors from crude oil stills and coke stills by means of a vapor separating device similar to the one shown in Fig. 40. This is intended to separate, in the vapor state, the vapors of naphtha and burning oil. Apparently the device is applicable to a number of cracking methods where gasoline and kerosene are simultaneously produced by the breaking down of heavy hydrocarbons.
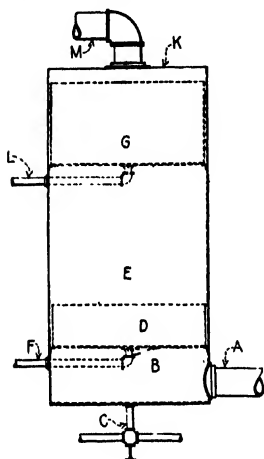
Fig. 40.

The vapors entering through the inlet pipe A fill the space B and in this space condensed material and heavy vapors, settle out and are drawn off through pipe C. The lighter vapors flow upwardly through the space surrounding the pan D (which rests upon brackets and is held in proper place by spacers.) In the vapor chamber E a further stratification of the vapors takes place, the heavier vapors going to the bottom of this space, that is, pan D and are drawn off by pipe F while the lighter of these vapors pass upwardly through the space surrounding pan G into the vapor space K (which includes the space inside of the pan G and the space above it). The heavier of the vapors in the space K are drawn off through the pipe L while the lighter of these vapors, and the gases present, are drawn off through the pipe M.

H. Hennebutte[2] introduces heavy hydrocarbon oils and lighter hydrocarbons in liquid form in a heated condition into heated heavy oil while the temperature of the latter is above the boiling point of the lighter hydrocarbons so that the latter are immediately vaporized and serve as a carrier to promote the distillation.

C. E. Lepley[3] finds that in the manufacture of straight gasoline by ordinary methods, the separation of gasoline from kerosene is not as sharp as could be desired, that is, a certain amount of gasoline remains in the more volatile portions of the kerosene distillate. In order to make a better separation and thus increase the gasoline yield, a stream of crude oil heated to 800°–900° F. (427°–482° C.) is downwardly directed in a direction counter current to the course which the gasoline vapors take in their passage through the vapor line.

[1] U. S. Patent 1,264,668, April 30, 1918.
[2] Chem. Abs. 1916, 692; U. S. Patent 1,165,878, Dec. 28, 1915.
[3] U. S. Patent 1,261,410, April 2, 1918.

The still A (Fig. 41) is charged with petroleum as in ordinary practice, and the distillation is conducted in the usual manner, until the tests indicate that the gasoline, and other products having relatively low boiling points, have been driven off to the extent to which this method of treatment is available. A downwardly directed stream of highly heated petroleum from the tank B, is then introduced into the tower C, such petroleum being of the same general character as the initial charge in the still itself. In order to produce this result, the petroleum in the tank B, is forced through the coil D, by means of air pressure and, in its passage through the coil D, is heated to a temperature from 800°–900° F. (427–482° C.), the pressure being about twenty pounds. The heat of the still proper is itself raised to a point preferably a little below that at which kerosene of the desired gravity for that particular product would go over freely, and, while thus heated, the stream of highly
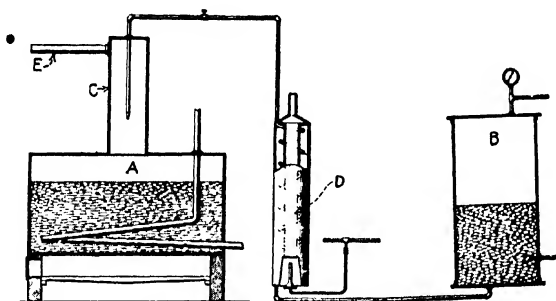
Fig. 41.

heated petroleum from the flue chamber D is injected in the direction to meet any vapor arising from the material in the still proper.

Under these conditions Lepley believes the following to occur. The vapors arising from the materials in the still consist of particles of gasoline and other light products, intimately associated with particles of kerosene, and if the application of heat were continued in the ordinary way, the composite particles would go over together, but by contact with the opposing stream of highly heated petroleum, injected under pressure, it appears that the more highly volatile portions of the stream associate themselves with the more highly volatile portions which are coming off from the material in the still, dissociating the latter from their intimate commingling with the kerosene or heavier constituents so that the lighter particles both from the still charge and the injected charge combine and pass off together through the vapor pipe E, while the less volatile portions of the injected stream associate themselves with the less volatile portions coming off from the material in the still and tend to drop back into the still.

It is stated that the temperatures employed vary with different kinds of initial material, but that with ordinary crude petroleum from the Caddo Fields, the initial distillation of the gasoline and light products can be properly effected at a temperature of 300° F. (149° C.) in the still, and that, without raising this temperature by means of the furnace or steam coil, the injection of the stream of vaporized petroleum at a temperature of from 800°–900° F. (427–482° C.) and under a pressure of about twenty pounds will give good results.

F. A. Kuhn [1] distills gasoline in order to refine it, in a vessel which is wholly immersed in a water boiler.

Dykema, [2] quoting from **Burrell**, gives the following figures on the latent heat of vaporization of petroleum distillates and condensates.

Gravities and latent heats of four distillates

	Gravity, °Bé.	Latent heat, B.t.u. per pound
Kerosene	43	105
Naphtha	56	103.5
Gasoline	65	100.6
Gasoline	89	100.2

In gasoline computations it is customary, it is said, to use as the latent heat 100 B.t.u. per pound. Kent is quoted as giving the specific heat of liquid gasoline of specific gravity 0.68 to 0.70 as 0.53 to 0.55, and " Lucke [3] quotes Regnault as stating that methane has a specific heat of 0.5929 at constant pressure and 0.4505 at constant volume."

E. W. Dean [4] states that the output of gasoline may be increased by universal adoption of higher distillation end-point, use of more efficient refining methods and wider use of cracking processes. High-test gasoline now marketed has an end-point of approximately 175° C. (347° F.). Usual grades fall between 200° and 230° C. (392°–446° F.). Universal adoption of the last temperature would increase the total yield 15 to 20 per cent. Efficiency of fractionation in refineries varies from 75 to 95 per cent. If all could approach the latter figure it would mean an increase of gasoline yield of perhaps 10 per cent. Burton's cracking process is considered, it is said, to be the only one in successful use today and it has limitations. Refining losses are about 4 per cent. By use of scrubbers and other recovery apparatus this loss should be cut to 2 per cent.

Wingett [5] proposes an automatically controlled still.

Drying Crude Oil and Simultaneously Recovering Naphtha.

Collins [6] dehydrates California oil by heating under pressure to destroy the emulsion, then gradually releasing the pressure. This is accomplished by allowing

[1] Chem. Abs. 1917, 1039; British Patent 102,903, Aug. 10, 1916.

[2] Recovery of Gasoline from Natural Gas by Compression and Refrigeration, Bureau of Mines Bulletin, 151 (1918).

[3] Lucke, C. E., Engineering Thermodynamics, 1912, p. 578.

[4] Chem. Abs. 1919, 905; Oil and Gas J. 1919 (17), No. 38, 52–3.

[5] U. S. Patent 1,229,189, June 5, 1917.

[6] U. S. Patent 1,028,439 June 4, 1912; see also Travers, U. S. Patent 1,004,219, Sept. 26, 1911.

the mass of petroleum and water vapor to expand or rise within a tall separating column. Naphtha is removed from the top of the column.

J. A. Dubbs [1] describes a process devised primarily for dehydrating crude oil containing water. The crude oil is pumped through a pipe coil which acts as a preheater and then through a larger coil or pipe still. Dehydrated oil flows from the pipe still into storage tanks.
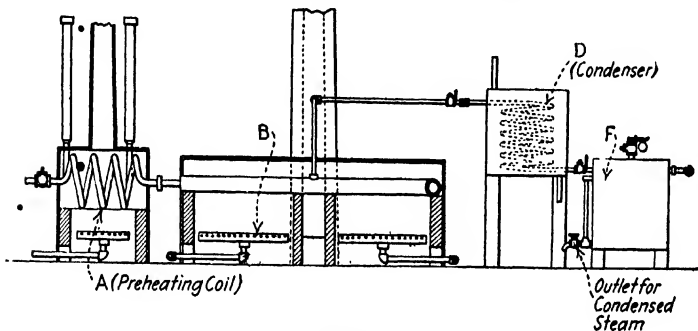
Fig. 41a.
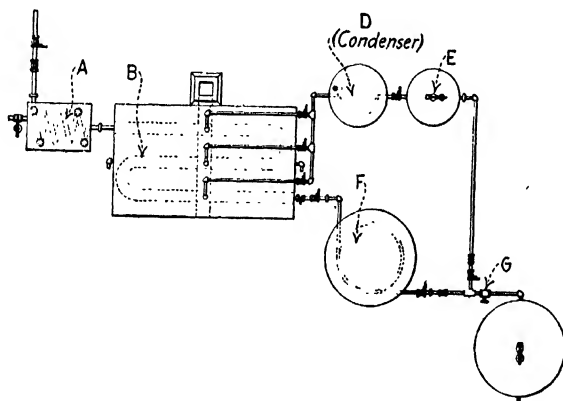
Fig. 41b.

The diameter of the pipe constituting the pipe still is such that there is a space above the oil as the latter is in process of dehydration and distillation.

As shown at B in Figs. 41a and 41b the pipe still comprises horizontally laid pipes connected together to form a continuous coil and the members of this coil are apparently in the same horizontal plane, which

[1] United States Patent 1,123,502, Jan. 5, 1915.

accounts for the fact that there is a vapor space above the oil during its passage through the pipe still.

Vapor pipes, in free communication with a condenser, as shown at D, remove steam and light distillate generated in the pipe still. It is important to note that the latter is in free communication, through vapor pipes with a condenser for steam and distillate and that, as in the Burton process, condensation takes place under pressure and also that the pressure generated in the still is caused by the vapor' tension of the hydrocarbons generated, although in Dubbs' method it would appear that much of the pressure is caused by steam evolved from water naturally contained in crude oil.

Figure 41a is a sectional elevational view and Fig. 41b a plan view of an apparatus suggested by Dubbs. D is a condenser for steam and light distillate and F a cooler for dehydrated oil. Throttle valve G, Fig. 41b, controls pressure in the distilling and condensing systems. E is a receiver which separates water from light distillate.

The apparatus is essentially a pipe still in which distillation takes place under pressure during the flow of oil. Oil does not completely fill the volume of the pipe still with the result that there is space in the pipes occupied by hydrocarbon vapors under pressure and the vapor space mentioned is in free communication with a condenser.

E. L. Dyer[1] dehydrates crude oil emulsions in a special tubular apparatus and simultaneously recovers naphtha.

Melchior[2] shows a special tubular device for dehydrating petroleum emulsions.

An apparatus consisting of a separator, two pumps, and four stills arranged in series is used by H. C. Leete,[3] for heating oils. The hot residue (fuel oil) from the last still passes through a pipe leading to one of the pumps and serves to preheat the crude oil, which is forced by the other pump through tubes extending through the fuel oil pipe and leading to the separator. The heated crude oil enters the separator under pressure and impinges against a deflecting plate, where it is atomized and gasoline is liberated. From the separator the oil, freed from gasoline, passes to the stills.

A pipe still designed so as to facilitate rapid cleaning is described by H. W. Jones.[4]

[1] U. S. Patent 1,207,381, Dec. 5, 1916.
[2] U. S. Patent 1,253,411, Jan. 15, 1918.
[3] J. S. C. I. 1919, 352 A; U. S. Patent 1,288,934, Dec. 24, 1918.
[4] U. S. Patent 1,336,357, Apr. 6, 1920.

CHAPTER V

REFINING METHODS— *Continued*

Processes Based on Evaporation

Evaporation processes are usually diametrically opposed to cracking. Their object is to vaporize the valuable constituents of an oil at as low a temperature as possible. They are often concerned with the treatment of sensitive oils like California crude.

Alexéjew [1] distills oils in a still with the aid of hydrocarbon vapors and gas which are injected into the oil, in the still. The mixed vapors
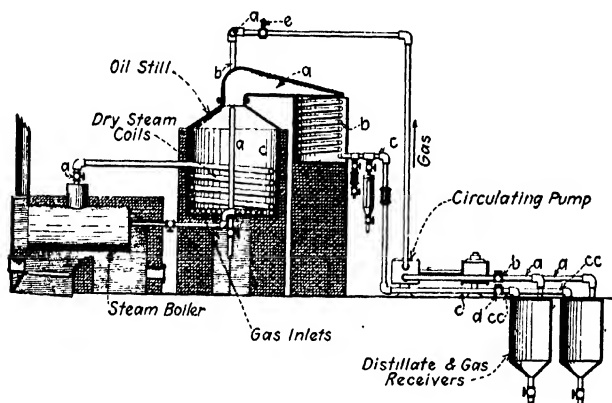
Fig. 42.— Process of Well and Wells

are passed through retorts and a condenser. Uncondensed gases are taken from the tail pipe and recirculated through the oil in the still.

W. C. Wells and **F. E. Wells** [2] describe a process for topping crude oils to remove naphtha and burning oil and leave a residue said to be of higher grade than that produced by ordinary methods. The oil is not boiled. Instead, its temperature is gradually raised by means of " dry " steam coils and a permanent gas is blown through the hot oil. For the removal of a fraction of any given boiling range the temperature

[1] Ber. 1887, 609; German Patent 39,949, Sept. 23, 1886.
[2] U. S. Patent 877,620, Jan. 28, 1908.

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of the oil is maintained considerably below that range and the evaporating effect of the gas and its mechanical carrying effect are depended on to volatilize and remove the vapors. In other words, " gas "[1] is used, instead of bottom steam.[2] The gas is circulated and used over and over again. (See Fig. 42.)

In another process of **Wells** and **Wells** [3] a permanent gas is used as before, but instead of heating with steam, the oil is heated by means of a fused bath. This is heated in still A (Fig. 43), constructed like a fire tube or shell boiler. The fused metal lies on the bottom of the shell and covers the fire tubes. Oil rests on the fused metal. A permanent
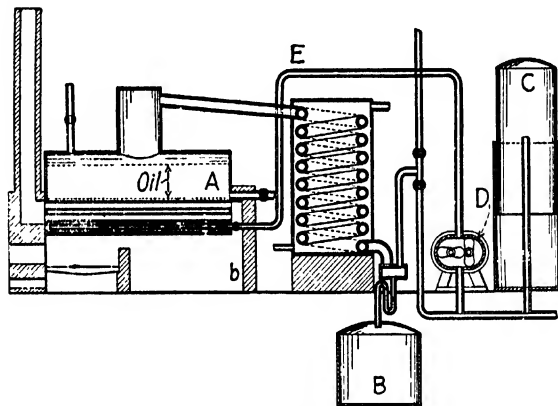
Fig. 43.

gas is blown through the oil by means of pumps D and conduit E and a perforated coil in the still. Gas and oil vapors pass through a condenser, condensate collects in B and the permanent gas is circulated back into the still. C is a gasometer.

F. H. Dunham [4] heats heavy asphaltic oils in a shell, pumps hot oil from the bottom of the shell and delivers it to the top of an evaporating chamber (A, Fig. 44). The lighter constituents of the oil evaporate here and are tapped off. The liquid residue flows back into the still and onto the surface of another evaporating pan in the still, and is here subjected to a sort of Soxhlet extraction. A vapor line conducts

[1] One of the authors has seen cases where the principle of this process has been used to good advantage in preparing a lubricating oil from a sensitive " crude."

[2] By the term " gas " a fairly permanent gas is meant, such as methane, although other and more easily condensable gases may be employed.

[3] U. S. Patent 1,296,244, Mar. 4, 1919.

[4] U. S. Patent 1,013,283, Jan. 2, 1912.

vapors from the still, or shell. The residue in the shell is asphalt or asphalt cement. This process appears to represent an attempt to simulate those conditions, in part, which produce natural asphalt. The element of oxidation, however, does not appear to play a very important part here.

M. J. Trumble [1] states that California oils and similar oils when repeatedly vaporized and condensed undergo cracking and that when naphtha and burning oils are contaminated with such cracked products discoloration results " when the contaminated oils are exposed to the actinic rays of light." He realizes that it requires a higher temperature
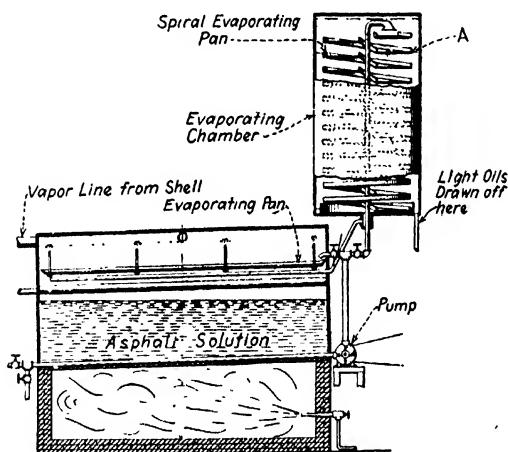
Fig. 44. — Dunham's evaporating method.

to vaporize a given liquid hydrocarbon out of solution in a body of oil of boiling point higher than that of the hydrocarbon in question, than is required to vaporize the pure liquid hydrocarbon.

The object is to avoid heating those hydrocarbons (naphtha and burning oils) any more above their boiling points than is necessary in order to separate them from the main body of oil (crude or reduced crude). This is accomplished by means of surface evaporation with the aid of heated gases, for example, steam.

It is stated that (referring evidently to California and similar oils) in order to avoid cracking these oils into unsaturated hydrocarbons it is necessary to appreciate the sensitive nature of (asphaltic) petroleum oils. Trumble's method consists in heating crude oil only to the point where, when this oil is finely divided, evaporation will complete

[1] U. S. Patent 1,070,361, Aug. 12, 1913.

the removal of the light oils from the heavy oils. The feature of his process is therefore his method of evaporation. Oil is first brought to the necessary temperature in a series of continuous retorts (Fig. 45). From the last retort in the battery it is lifted to the top of the evaporating chamber (Figs. 45 and 46) or tower. Inside the tower the heated oil falls through perforated baffles on to spreading cones and flows in a film down the inside of the tower. The latter is heated to about the same temperature as the entering oil. Evaporation comes into play, light oils are vaporized and pass out of the tower through holes in the central vapor collecting pipe. Steam, injected at the base of the tower,
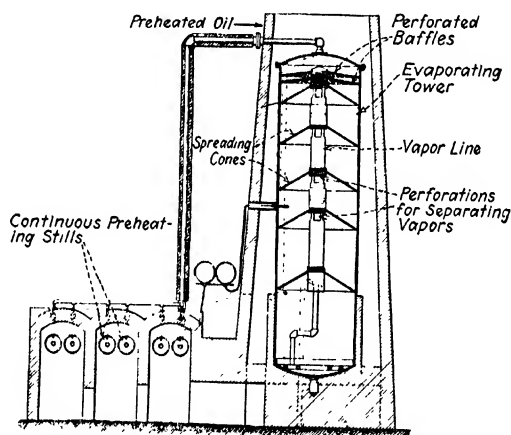
Fig. 45. — Trumble refining system.

assists the evaporation. The light oils pass through a vapor collector (Fig. 46) to a condenser and heavy residues collect at the base of the evaporating tower.

More recently **Trumble** [1] describes another system proposed for the continuous and rapid vaporization of light oils from California crude by " surface " distillation or evaporation.

Crude oil is pumped under slight superatmospheric pressure through heat interchangers and then through heating coils (Fig. 47). From these it expands through a reducing valve into the top of a tall expansion and separating chamber. The light oils, now at a temperature above their boiling point at atmospheric pressure, are suddenly converted into vapor. These vapors and condensed oils flow down along the sides of the chamber on account of baffle plates interposed as shown, and any

[1] J. S. C. I. 1918, 330 A; U. S. Patent 1,262,875, April 16, 1918.
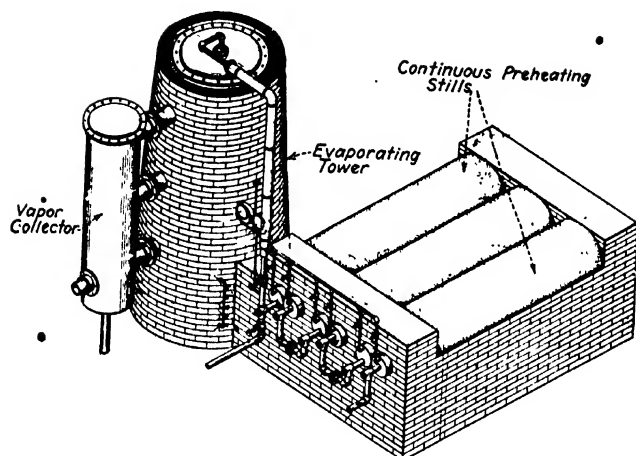
Fig. 46. — Trumble refining system.
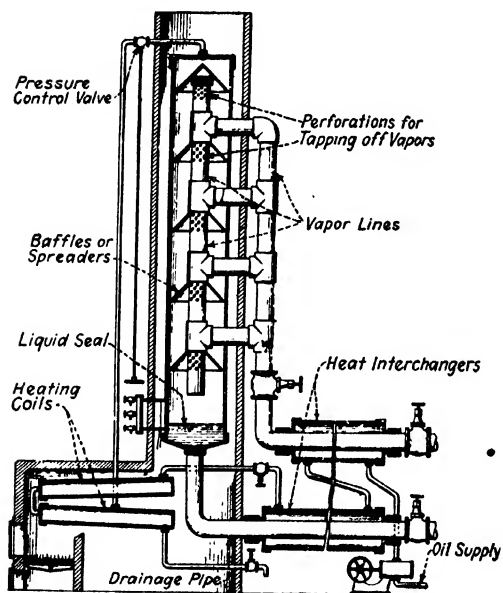
Fig. 47. — Trumble refining apparatus.

liquid oils are thus spread out into thin films. Surface evaporation and boiling then take place. The uncondensed vapors pass off through perforations in a central pipe. Vapors of different gravities are thus tapped off at different points in the vapor line. Heavy oils collect at the bottom of the separating chamber and are tapped off through a drainage pipe.

N. W. Thompson,[1] in a detailed description of the Trumble refining process, states that the plant described uses as fuel 1.1 per cent of the crude oil run through it, with refining losses of only 0.75 per cent.
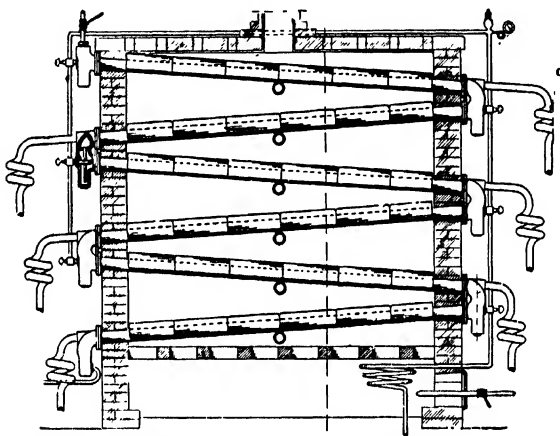
Fig. 47a. — Pipe still, proposed by Burleson and Prutzman.

R. G. Jones[2] evaporates California oil in a series of pan-shaped units situated one above another in a heating "stack" or tower. Vapors are withdrawn from each unit as the oil flows downwardly.

A form of pipe still for evaporating and separating petroleum into its fractions, as suggested by **Burleson** and **Prutzman,**[3] is shown sectionally in Fig. 47a. The tubes are D-shaped and set with the flat side down and exposed to the heat, the rest of the tube being insulated to guard against "cracking" of the vapors. Each return bend connection is provided with a trap intended to prevent vapors from passing from one tube to the next. In this way, vapors distill out of each tube in the series.

The idea is to have a thin film of oil flowing along the flat surface of the tube, and to withdraw vapors of different density at the various

[1] Chem. Abs. 1917, 3424; J. Am. Soc. Mech. Eng. 1917 (39) 831–4.
[2] U. S. Patent 1,166,375, Dec. 28, 1915.
[3] U. S. Patent 1,180,237, April 18, 1916.

points in the tube system. Steam is also used to assist in the evapo-
ration and to protect the vapors from cracking.

T. E. Murray and **E. B. Ricketts** [1] coke reduced crude oil by spread-
ing it in a continuously flowing film over the inside of flues through
which hot gases are passing counter currently.

A, Fig. 48, is a cylindrical still shell, open below and supported above a pit
B which contains water, into which the lower end of the shell enters. On one side
of the shell is a chamber *C*, into
which enters a gas burner *D*, the
heated gas current from which passes
upwardly through the shell and es-
capes at the duct *E*, which opens into
shell *A* through the head *F*.

Above the shell is a ring duct *G*
which by pipe *H* communicates with
a source of supply of the crude oil
residuum to be coked. Depending
from ring *G* and passing through head
F are a number of short delivery pipes
I. The outlet ends of these pipes are
flared, and the ends are turned hori-
zontally, so that the escaping re-
siduum is projected from each of these
pipes *I* against the inner surface of
shell *A*, and then flows downwardly
along the surface in a thin layer.
The thin layer of residuum is acted
upon by the ascending current of
hot gas from burner *D*, and because
of its thin or film-like character, the
volatile products — in the case of
crude oil residuum, fuel oil and wax
tailings — are rapidly evaporated,
and pass off by duct *E*. The coke is
deposited upon the inner surface of
the shell, and can be readily detached
by percussion on the outside of the
shell, so that it falls off and drops
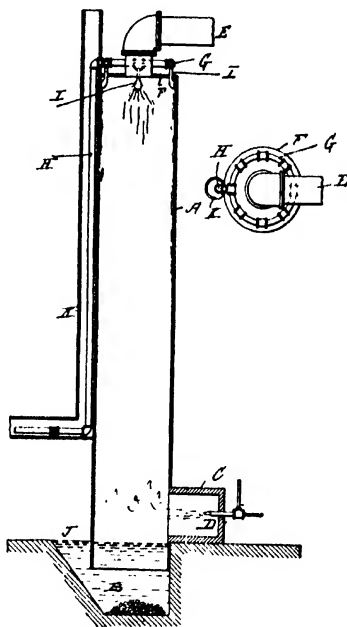
Fig. 48. — Method of coking oil proposed by
Murray and Ricketts.

into the water in pit *B*. The object of flaring the ends of delivery pipes *I* is to pro-
ject the residuum as flaring or expanding jets, and in this way insure that the
layer, sheet or streams which flow down the inner surface of the shell shall be
thin, and readily volatilizable by the hot gas. The pipe *H* is surrounded by a
jacket *K*, through which may be passed hot gas.

[1] U. S. Patent 1,293,866, Feb. 11, 1919.

REFINING METHODS — *Continued*

Forward's Processes

Forward's methods endeavor to reduce crude oil in such a way as to continuously secure naphtha which needs little or no chemical treatment. They are based, in part, on the principle of vaporizing the oil and effecting separation by fractional condensation. Superheated steam is the heating medium.

Forward [1] atomizes crude oil with superheated steam and injects the mixture into a shell where a high pressure and an elevated tem-
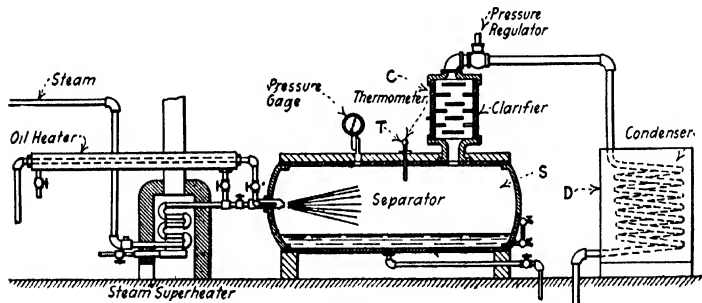
Fig. 49.

perature may be maintained. This separator (Fig. 49) is provided with a superimposed dephlegmator (*C*). Just beyond the dephlegmator there is a relief valve which may be set, say, at 100 pounds. An excellent separation of light and heavy oils is said to take place, and by reducing crude oil in this way, there is stated to be obtained, in one operation, an unusually large yield of commercial naphtha. This process evidently aims at producing a commercial gasoline or naphtha in one operation, which, without further treatment with acids and alkalies is "acceptable to the trade."

Following this, Forward brought out a number of improvements. That shown in Fig. 50 [2] consists in continuously subjecting the crude oil residue from one " separator " to retreatment. Four separators are shown in series, each provided with a superimposed dephlegmator or

[1] Chem. Abs. 1916, 2144; U. S. Patent 1,189,083, June 27, 1916.
[2] J. S. C. I. 1916, 1254; U. S. Patent 1,202,823, Oct. 31, 1916.
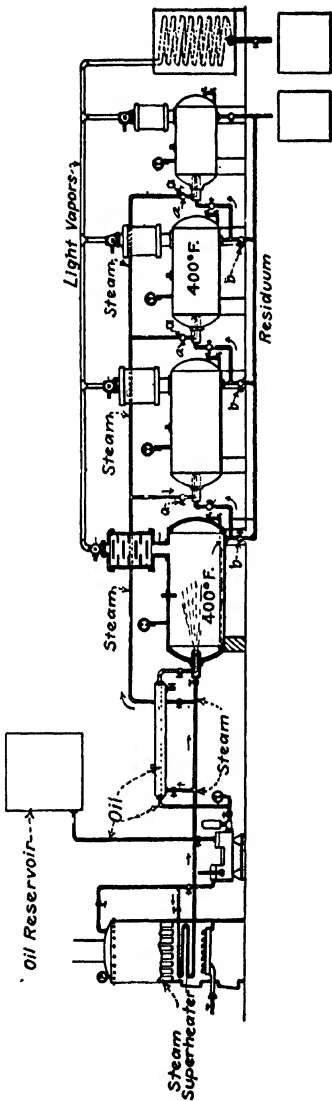
Fig. 50.

" clarifier." The residue in the first separator in the series is retreated in the same way and under about the same conditions, in the second separator in the series, and so on. The pressure in the separators and dephlegmators is 50 pounds or higher and the temperature approximately 400° F. (about 200° C.).

A still further improvement [1] consists in maintaining an increased temperature and pressure in each successive separator. This is done by admitting to each separator an increased volume of superheated steam. This in turn is done by using, in addition to the nozzle in the front of each separator, a steam injector as shown at A (Fig. 51) which permits the use of a much larger volume of steam and also mixes the residue from the next preceding separator with fresh superheated steam before the mixture passes through the nozzle (B).
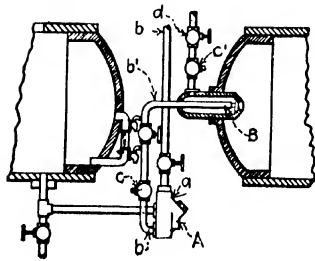
Fig. 51

Recently Forward [2] has proposed a method for obtaining in a single operation (without filtration or re-running or treatment with acid and alkali), water white gasoline suitable as motor fuel. This consists in pumping oil to be stripped, for example, crude oil, through three independently heated sets of pipe coils, under high pressure and discharging the heated oil, atomized with superheated steam into a separating drum (Fig. 52) where pressure is also maintained.

Each coil of pipe is located in a high pressure drum (A, B, C, Fig 52). Highly heated high pressure (200–300 pounds) steam is admitted to drum C and flows consecutively to drum B and A, with a consequent decrease of temperature and pressure in each drum. Residuum collects in the bottom of the separator and volatile hydrocarbons and steam pass into a series of dephlegmators. Further separation takes place here and refined motor fuel is said to be finally obtained after removal of condensed water.

Forward has also designed a number of processes for recovering, in one operation, a high yield of gasoline from crude oil, which involve atomizing and vaporizing the oil in retorts by means of superheated steam and then effecting the separation of the various fractions by fractional condensation.[3] Fig. 53 [4] shows a retort setting for one of these processes.

[1] U. S. Patent 1,274,405, Aug. 6, 1918.
[2] U. S. Patent 1,299,449, April 8, 1919.
[3] U. S. Patents 1,088,693, March 3, 1914; 1,181,301, May 2, 1916; 1,247,808, Nov. 27, 1917; 1,255,149, Feb. 5, 1918.
[4] U. S. Patent 1,255,149, Feb. 5, 1918.

Fig. 52
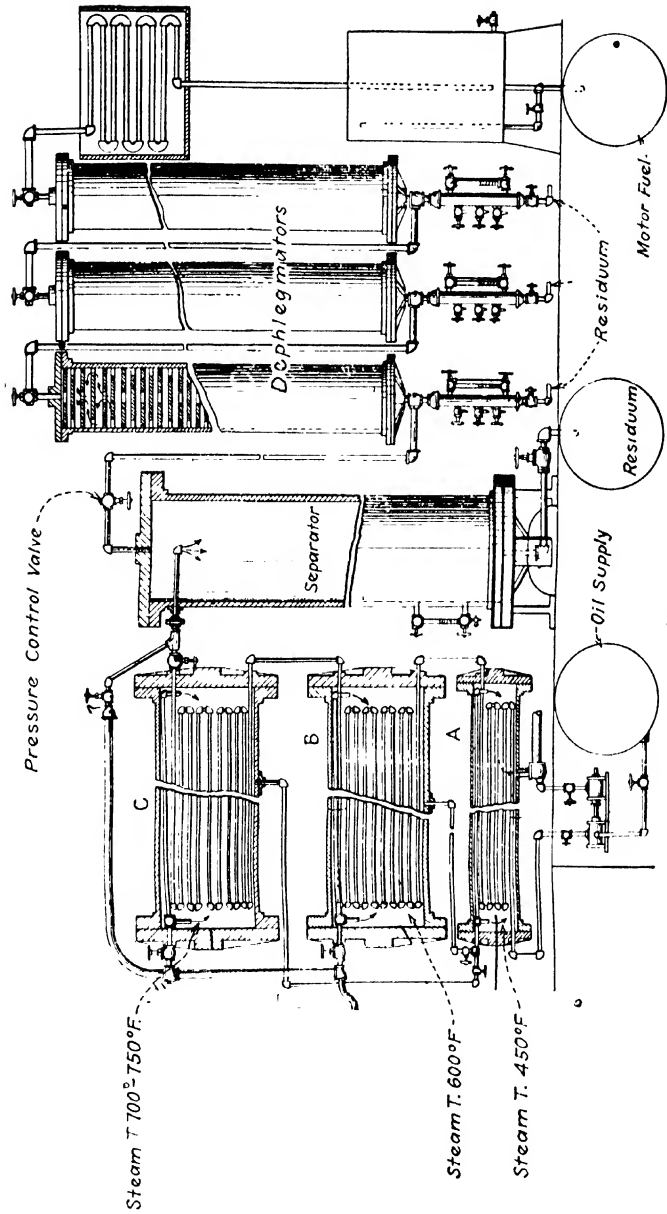
In Fig. 53, the vaporizing retorts are shown at *A* provided with
jackets for superheated steam. Steam is superheated in coils located
in the fire box beneath the retorts. The steam pipe conveying super-
heated steam then emerges from the interior of the furnace and leads
to a distributing header in the front of the furnace. From this header
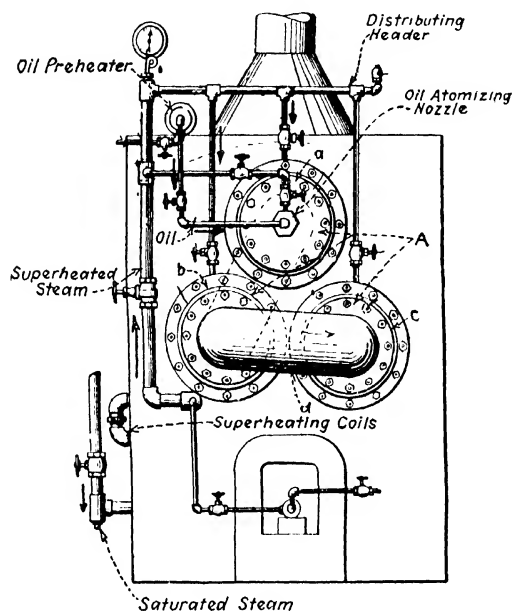
Fig. 53.

superheated steam is delivered to the jacket of each retort. The re-
torts are connected in series.

Oil is pumped through an oil preheater on top of the furnace where
superheated steam accomplishes the preheating. The oil is then in-
jected by means of superheated steam to the uppermost retort, passes
through all the retorts and progresses to dephlegmators for the recovery
of naphtha.[1]

[1] See also C. B. Forward, British Patent 117,372, Oct. 27, 1917 French Patent
481,494, Dec. 8, 1916, U. S. Patent 1,247,808, Nov. 27, 1917.

CHAPTER VII

DISTILLATION UNDER PRESSURE[1]

The distillation of heavy oils under pressure has furnished a considerable portion of the output of "cracked" gasoline in the United States. It is contended by some that the method of distilling and condensing under pressure, as practiced by a very large oil company, yields the smallest amount of uncondensed gas per gallon of "gas naphtha" produced, of any of the cracking processes commercially practiced for the production of gasoline at the present time. The method referred to has assumed very large proportions in the last ten years and this is proof in itself that the early difficulties encountered were not insurmountable. In the original Burton process (Chap. X) only about one-third of the charge of oil could be distilled, according to **Humphreys**,[2] owing to the accumulation of carbon deposit on the still bottom. One of Humphreys' improvements consists in equipping the still with a number of false bottoms (see Fig. 54). It is natural that the original method should have become considerably modified as experience, in the hands of skilled operators, was gained. Effort is made herein to show the nature and trend of these developments.
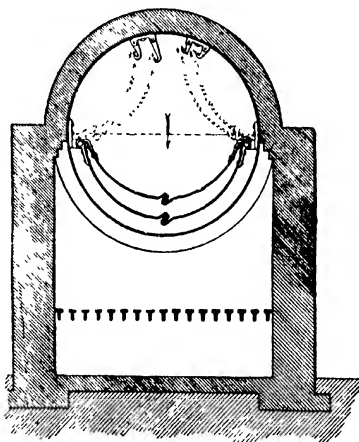
Fig. 54 — Humphrey's modification of the Burton still.

[1] See also chapter on Burton process.
[2] U. S. Patent 1,122,003, Dec. 22, 1914.

Early Experiments and Processes in Decomposing Oils by Distillation [1]

In 1805, as well as in 1821, **Henry** [2] described the gas obtained by cracking animal oils, fats and waxes, noticing the formation of ethylene. In 1865 **Young** [3] took out a patent for increasing the yield of burning oils by distillation under a pressure of about 20 lbs., which was followed in 1866 by that of **Vincent** and others [4] in which the vapors were partly cooled at the still-head, the condensates being allowed to fall back on the hot residues; and a provisional patent in 1869 by **Scot** and **MacIvor**. [5]

In the meantime, the question was being discussed by **Hirsch**, [6] **Stillman**, [7] and **Peckham**, [8] from a theoretical standpoint; an account of his process was published by Young in 1867, [9] which was followed in 1871–1873 by the famous researches of Thorpe and Young [10] on the effect of distilling solid paraffin under pressure, together with a description of products formed, boiling below 200° C., these products consisting of paraffins and olefins as follows: — amylene, pentane, hexylene, hexane, heptylene, heptane, octylene, octane, nonylene, nonane, undecylene, undecane and possibly caprylidene, but with no trace of benzene.

Studying methods of increasing yields of illuminating oils from petroleum **Lisenko** [11] found that when petroleum is distilled, it is not only split up into its constituents, but certain parts of the higher-boiling fraction are decomposed into bodies of lower boiling point, the yield of these varying with the time of heating. By heating residues from Caucasian petroleum at 434°–501° C. (813° 934° F.) the yield of kerosene was increased by 30 per cent.

Benton [12] heated oil under pressure (500 pounds) to a temperature of 371° 537° C. (700°–1000° F.) and then expanded the reaction product, in order to increase the yield of burning oil.

[1] From a discussion by **Lomax**, J. Inst. Petroleum Technologists, 1916 (3), p. 36, *et seq.*
[2] Journ. Nat. Phil. Chem. Arts, 2 (xi), 65: Phil Trans. 1821, 136.
[3] British Patent 3345 (1865).
[4] Vincent, Richards and Others, British Patent 616 (1866).
[5] British Patent 2588 (1869).
[6] Chem. News, 1868, xviii, 51.
[7] Amer. Journ. Sci. 1867 [2], xliii, 242.
[8] Amer. Journ. Sci. 1869 [2], xlvii, 9.
[9] Polyt. Jour. 1867, clxxxiii, 151.
[10] Proc. Roy. Soc. 1871–1873; xix, 370; xx, 488; xxi, 184.
[11] Gorn. Journ. 1887 [ii], 349; Polyt. Journ. 1887 [cclxvi], 226.
    U. S. Patents 342,564 and 342,565 (1886).

In 1889 **Redwood** and **Dewar** [1] patented their well-known process for increasing the yield of light oils from residues by distillation and condensation under pressure. This process gave very good results. It was designed with a view to increasing the yields of kerosene from Russian oil, and thus decreasing the amount of ostatki produced, which was then somewhat of a drug on the market, but the employment of ostatki as a fuel came into prominence about this time, and it became as valuable as the kerosene which was produced from it, and so the process was abandoned for the time at least.

In 1893, **Engler** and **Singer** [2] obtained solid paraffin of m p. 49°-51° C. (120°-124° F.) by the dry distillation of fish oil, and in 1897 **Engler,** [3] by distilling animal fats under pressure, obtained oils containing little nitrogen which were however of light gravity and low boiling point, and did not account for the oils of high gravity, molecular weight and boiling point found in petroleum. He proposed to ascribe the production of these higher compounds to the gradual polymerization of the lower ones, and gave instances of small increases of specific gravity on standing. In the same year, along with **Lehmann,** [4] he examined the products of the distillation of fish oil under pressure, identifying the olefins from hexylene to nonylene, paraffins, benzene, toluene, metaxylene, mesitylene and pseudo-cumene, while the presence of naphthenes was not conclusively proved. In another paper he showed, in conjunction with **Jezioranski, Grüning** and **Schneider,** that the residues from the distillation of petroleum boiling above 200° C. (392° F.) decomposed on heating in open vessels or under pressure, giving the lower members of the paraffin and olefin series from C_6 to C_{10}, along with aromatic hydrocarbons and some naphthenes, but when heated *in vacuo* distilled without decomposition. Later in 1906 **Engler** and **Rosner** [5] examined the gas produced in the cracking of Baku crude oil, finding it to consist mainly of methane, ethane, hydrogen, and unsaturated hydrocarbons.

Krämer and **Spilker** [6] in 1900 gave the results of distilling Baku residues at 450° C. (842° F.) under 20 atmospheres pressure, light oils being formed; and in 1901 **Edeleanu** [7] obtained aromatic hydrocarbons by superheating certain fractions from Rumanian crude oil, while **Singer** [8] in 1903–1904 showed that with Rumanian petroleum cracking

[1] See **Dewar** and **Redwood**, Chap IX
[2] Ber. 1893, xxvi, 1449.   [3] Ber 1897, xxx, 2358.   [4] Ber 1897, xxx, 2365.
[5] Allg Osterr. Chem.-Techn. Zeit. 1906, xxiv, No. 9.
[6] Ber. 1900 [xxxiii], 2265
[7] Chem Rev Fett-Harz-Ind 1901 [viii], 63.
[8] Chem. Rev. Fett-Harz-Ind. 1903 [x], 271; 1904 [xi], 3.

takes place at as low a temperature as 200°–300° C. (392°–572° F.).
Ipatiev, in 1904,[1] stated that in the distillation of petroleum under
pressure, at the higher pressures the evolved gases become continually
poorer in hydrogen, in spite of the higher temperatures required to
maintain the higher pressures. The pressures employed in his work
were from 120–340 atmospheres.

The Development and Refinements of the Method

B. B. Freud,[2] referring to pressure distillation, says that if "crack-
ing" is done at "higher pressures" the amount of olefins is less.
Likewise at higher pressure, in spite of the higher temperature neces-
sary to maintain it, the amount of hydrogen in the evolved gases is
less; hence the simultaneous use of higher pressures with high tem-
peratures to get a product richer in saturated hydrocarbons than is
obtained by the use of high temperature alone. Whether, it is stated,
the smaller amount of olefins is a result of hydrogenation under the
new conditions as is plausible from the work of Whitaker and Rittman,
or whether the saturated hydrocarbons are formed simultaneously
with the appearance of the dissociated hydrogen and olefin (or alkyl-
idene) as is indicated by Bacon, cannot be determined at present.

Krey,[3] according to **Graefe** and **Walther,**[4] distills heavy oils under
pressure of 2–6 atmospheres in order to obtain illuminating oil.

A. Riebeck's Mining Works, Inc.,[5] distills heavy oils under pressure
to produce naphtha and burning oil, and places the control valve be-
tween the still and condenser.

J. Laing[6] proposes to crack heavy oils by repeated distillation or
volatilization and condensation under a pressure not greater than ten
pounds per square inch. A sectional view of the apparatus used for
this purpose is shown in Fig. 55. The still is internally divided into
compartments by partitions extending from the top downward to
within about sixteen inches of the bottom. A series of condensers are
provided one for each compartment. The idea is to distill oil from
one compartment to the next and finally have it pass out through the
gooseneck shown on the right hand. In each succeeding compartment
of the still, it is said, more and more light oil is found, the largest
amount accumulating in the compartment B^4. Possibly the purpose

[1] Jurn. Russk. Phiz. Khim. Obsch. 1904 [xxxvi], 786; Ber. 1904 [xxxvii], 2961.
[2] The Chemical Engineer, 1915 (21), 161.
[3] German Patent 37,728 (1886).
[4] British Patent 25,510, Nov. 7, 1913.
[5] German Patent 37,728, Klasse 23, Feb. 28, 1886.
[6] British Patent 4120, March 17, 1890.

is to combine in one still the action of several stills. The equipment is designed to heat each compartment to a progressively decreasing degree.

Soon afterward[1] Laing interposed a vapor cracking chamber between the gooseneck and condenser and at about the same time also proposed[2] placing a loaded valve between the still and the condenser and a cooled expansion chamber just beyond the loaded valve. Laing did not condense under pressure.

Subsequently[3] Laing states that the condensers attached to the several compartments were not as satisfactory as could be desired,
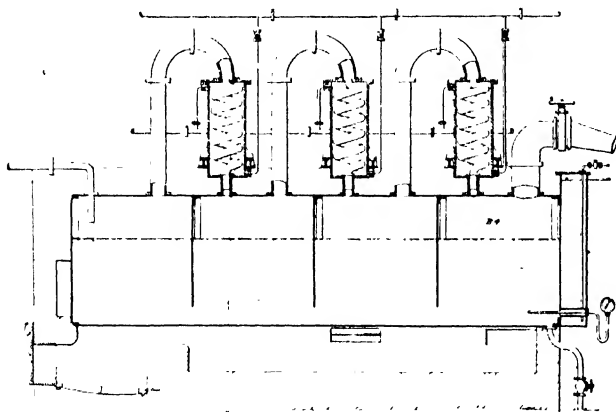
Fig 55. — Laing's still.

first because the cold oil from a condenser running into the hot oil in the compartment immediately beneath it cooled down the boiling oil in that compartment and interfered seriously with the process of distillation, and secondly that any water in the oil would be vaporized, condensed and then, in the form of cold water, be admitted to the boiling oil in the corresponding compartment, with serious results. This is improved by trapping the reflux condensates, separating the water and then more gradually heating the oil before allowing it to flow into the still again.

The process of **Halcour** and **Pilgram**[4] is said by **Graefe** and **Walther**[5] to involve distillation under pressure with the aid of inert gases.

[1] British Patent 11,079, July 16, 1890.
[2] British Patent 11,757, July 28, 1890.
[3] British Patent 23,446, Oct. 24, 1911.
[4] German Patent Application Class 23 B L 32,413.
[5] British Patent 25,510, Nov. 7, 1913.

Graefe and **Walther** [1] instead of distilling at moderate pressures and condensing under pressure, seek to obtain saturated low boiling hydrocarbons from heavy oils by distilling under very high pressure (40–50 atmospheres). A heavily constructed retort (Fig. 56) is heated by a bath of melted lead. The regulating valve A is *between* the retort and condenser. B is a valve for controlling the discharge of residue. The process is intended to be continuous, that is it is intended to pump oil into the retort and withdraw residues, without discontinuing the application of heat. The use of such high pressures
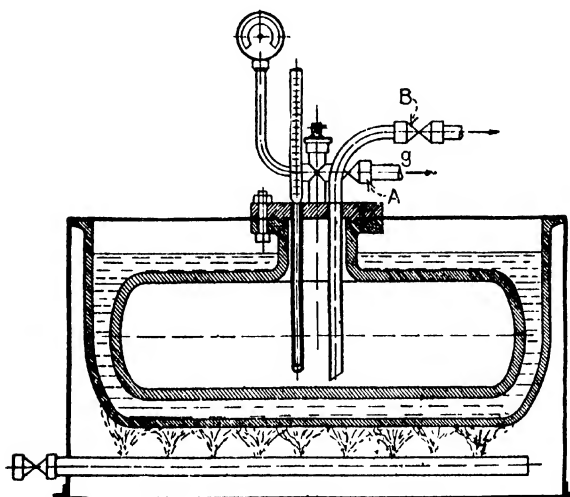
Fig. 56. — Pressure still proposed by Graefe and Walther.

would appear to necessitate limitation to apparatus of small dimensions. The best raw material is said to be distillation residues free from gasoline and illuminating oil, such as German, Californian, Mexican or Galician still residues.

Von Groeling [2] effects cracking in a column still to which preheated oil is admitted by spray-producers and which is heated by pipes through which circulates oil heated in a horizontal still under a pressure greater than that obtaining in the column still. A pump fills the horizontal still with crude oil at the beginning of the operation, and afterwards supplies sufficient residual oil from the base of the column "still" to

[1] British Patent 25,510, Nov. 7, 1913.

[2] J. S. C. I. 1915, 1045; Chem. Abs. 1916, 273; British Patents 10,213, 1913; 16,713, July 13, 1918, 4; U. S. Patent 1,295,08 Feb. 18, 1919.

maintain the requisite pressure in the horizontal still. The oil is circulated through the horizontal still and heating pipes by means of a pump, and a regulated quantity is allowed to escape through a pipe into the column " still " where it vaporizes. Superheated steam is also admitted at the base of the latter.

Von Groeling [1] distills oil with steam and passes the vapors through cracking tubes (F', Fig. 57). Cold oil, under a gravity head of pressure (from a supply tank not shown) passes through these cracking tubes in a direction counter to the direction of the vapors. Both the liquid
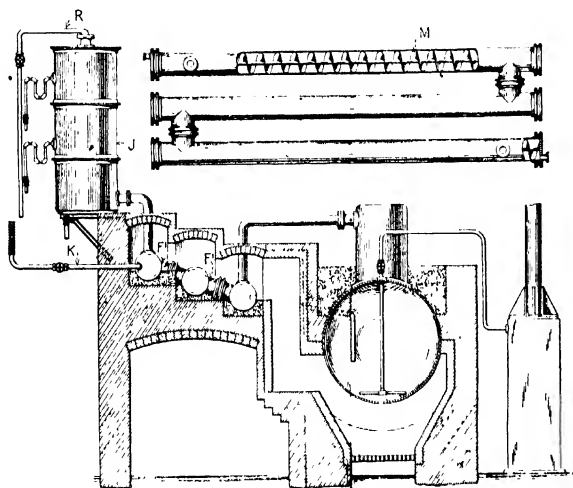
Fig. 57. — Still, heat exchanger and dephlegmator, according to on Groeling.

and vapor phases are therefore present in the tubes; and cracking and distillation take place simultaneously. The tubes are constricted by means of a worm M. Owing to the resistance to flow offered by the restrictions in the tubes (and in the dephlegmator J also) a pressure of about 1.5 atmospheres and a corresponding temperature is said to prevail in the still and tubes. Fresh oil enters the uppermost tube through the supply pipe K.

The vapors and gases pass to a dephlegmator J, provided with pans, which separate the vapors and gases into condensates of different gravities. Uncondensed gases escape through the pipe R on the top of the dephlegmator. The tubes F' act as heat exchangers as well as in a cracking capacity.

[1] British Patent 10,213, April 30, 1913.

R. F. Bacon and **C. W. Clark** [1] have found that the yield and quality of gasoline begins to decrease at pressures below 100 pounds in the still. They have found that about 300 pounds is the upper limit for practical purposes. The apparatus used is shown in Fig. 58.

They state that within certain approximate limitations of pressure, the yield of gasoline will be materially greater than when the distillation is effected under pressures above and below such limitations; and aside from the lower yields of gasoline, that the economic conditions of operation are prejudicial when effected both above and below these limitations of pressure. As far as the increase in gasoline yield is concerned it may be stated that a mixture of hydrocarbons of boiling points ranging from about 30° to 150° C. (86°–302° F.) at atmospheric pressure, that is, low boiling point hydrocarbons, may be obtained in relatively large quantities from
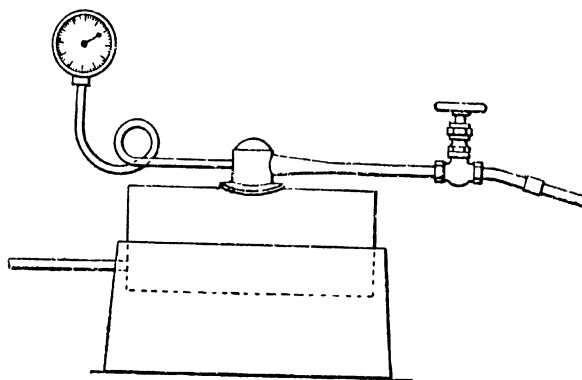
Fig. 58.

hydrocarbons of boiling points of about 250° C (482° F) and upward at atmospheric pressure, in other words, from high boiling point hydrocarbons, by distilling these high boiling point hydrocarbons at a pressure ranging from about 100 to 300 pounds per square inch. Bacon and Clark observed that not only are large quantities of low boiling point hydrocarbons obtained by distilling high boiling point hydrocarbons at a pressure ranging from about 100 to 300 pounds per square inch, but the quality, also, of the low boiling point hydrocarbons thus obtained is better for commercial purposes than that obtained by distillation at pressures below 100 pounds. The percentage of saturated hydrocarbons is greater when distillation is effected at pressures above 100 pounds than at pressures below it, and is practically a constant quantity at distillation pressures above about 100 pounds. Consequently, the subsequent refining loss, due to the presence of the unsaturated hydrocarbons, which yield tar by the action of the refining acid, is lessened. This loss, which is fairly uniform with gasoline resulting from distillation at 100 pounds pressure and upward, increases rapidly with gasoline resulting from distillation at pressures ranging downwardly from 100 pounds. The operator, in establishing the pressure prevailing within the still within the described range, likewise pro-

[1] U. S. Patent 1,101,482, June 23, 1914.

vides for such rate of distillation as will give at least the minimum proportional yield of low boiling hydrocarbons desired. Thus, for commercial purposes, may be taken at say 18 per cent by volume, of saturated hydrocarbons.

In determining the approximate lower limit of 100 pounds pressure per square inch, it is stated that when high boiling point hydrocarbons are distilled at a pressure below about 100 pounds, there is a relatively small yield of low boiling point hydrocarbons as compared with that obtained by distillation at a pressure above 100 pounds, all other conditions being the same. Furthermore, such yields of low boiling point hydrocarbons as may be obtained at a pressure below about 100 pounds are effected only at such sacrifice of time and fuel as to render working at such low pressures uneconomic and impractical. In determining the upper limit of about 300 pounds per square inch, above this distillation pressure there is not only a dropping off of the percentage of obtainable low boiling point hydrocarbons, but the still becomes coated with coke so rapidly that its heat conductivity is diminished and there is a constant liability of its blowing out. Also, the loss of hydrocarbons through gasification when distilling at pressures above approximately 300 pounds is a prejudicial factor.

The temperature depends upon the character of the high boiling point hydrocarbons treated. The temperature in each instance is such as to keep the mass, which is being distilled, under a pressure of from about 100 to 300 pounds. As an example of the temperature which may be required, a reduced Oklahoma petroleum (having had its gasoline and kerosene components removed from it) distills under a pressure of about 200 pounds at a temperature ranging from about 350° to 500° C. (662°–932° F.). In order to obtain the desired low boiling point hydrocarbons from the distillate thus produced, it is subjected to the ordinary fractional distillation at atmospheric pressure, subsequently to the distillation under pressure.

It is stated that it has been possible to obtain as much as 42 per cent of gasoline, that is, hydrocarbons boiling at a temperature ranging from about 30° to 150° C. (86°–302° F.) at atmospheric pressure, from hydrocarbons which before being subjected to the treatment contained no low boiling point hydrocarbons. This increase in the yield of low boiling hydrocarbons is not nearly so great when the mass of high boiling point hydrocarbons is first heated for a considerable length of time in a closed still or other receptacle to a pressure between 100 and 300 pounds per square inch, and subsequently distilled at about atmospheric pressure, as when the distillation is effected under the prescribed limitations of pressure.

G. P. Lewis [1] heats oil in the lower part of a vertical cylindrical apparatus by an external steam or hot gas jacket and the vapor passes upwards into a cracking chamber which contains a set of baffle plates and is heated externally by a steam or hot gas jacket, or internally by heating coils. The temperature of the heating medium varies from 400°–500° C. (752°–932° F.) and the pressure of the oil gas from 60–280 pounds per square inch. The cracked vapor passes upwards to a tubular condenser cooled by water at about 150° C. (302° F.). The temperature of the water is varied by a pressure control valve.

[1] J. S. C. I. 1916, 1101; British Patents 12,188, Aug. 24, 1915 and 2509, Feb. 19, 1916.

Uncondensed gases or hydrogen or both may be introduced into the cracking chamber.[1]

Chamberlain [2] in cracking under pressure [3] to obtain both gasoline and kerosene finds that fuel or gas oils (oils having an Engler viscosity of seventy seconds to one hundred and seventy seconds at 100° F. in an Engler instrument in which water has a viscosity of fifty-three seconds at the same temperature) do not give in his process such large yields of gasoline and water white kerosene as the entire heavy paraffin distillate yields, on pressure distillation at about seventy-five pounds.[4]

Chamberlain states that the entire heavy paraffin distillate obtained in the distillation of crude petroleum, treated with sulphuric acid and alkali, and retaining its content of paraffin wax, can be distilled under superatmospheric pressure with the production of what may be called high pressure distillate yielding a large proportion of finished naphtha with boiling points up to 338° F. (170° C.) (more than is obtained from high pressure distillate produced by distilling gas oils or fuel oils under like conditions), and also a large proportion of kerosene of better quality than oil distilling over between the same limits of temperature, 338° F. to 518° F. (170°-270° C.) which have been obtained from the high pressure distillate produced by distilling gas oils or fuel oils under like conditions. The kerosene from heavy paraffin distillate, according to Chamberlain, is lighter in gravity and lower in viscosity than that from gas oils or fuel oils and has also proved itself superior to the latter in burning tests, not exhibiting the same tendency as the latter to smoke, to produce a hard crust on the wick or to throw out mushroom-shaped formations of carbon on the wick. This improved quality of kerosene is of special importance on account of the scarcity of high quality oil which could be used to mix with inferior oil in order to increase the yield of a desired standard

Heavy paraffin distillate in each of four forms, that is to say, either pressed or unpressed and either treated or untreated with sulphuric acid and alkali, can be distilled under pressure, although not for all of the forms with the same advantage Such heavy paraffin distillate in each form contains liquid hydrocarbons with viscosities normal to heavy and medium grades of lubricating oils and also hydrocarbons with the intermediate viscosities mentioned in such relative proportions that in the distillation under pressure the decomposition of the hydrocarbons of each kind is modified by the presence of the other kinds. For exerting this modifying effect the hydrocarbons of any of the kinds should not be less than about ten per cent by volume of the sum total and in the distillate mentioned the kind present in least proportion is in excess of ten per cent. This distillate is also so far free from still wax and like heavy matters of sticky character or coke that charges of the distillate of practical size can be distilled under a superatmospheric pressure of seventy five pounds to the square inch to the extent of fifty per cent or more by volume without heating the still bottom to redness.

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[1] See also Lewis, British Patent 7535, May 19, 1915.

[2] J. S. C. I. 1917, 541 A; U. S. Patent 1,221,790, Apr. 3, 1917.

[3] Condensation does not take place under pressure. Pressure in the still is built up and maintained by a valve in the vapor line.

[4] The statement is made that, in distilling under pressure, the vapors evolved should not be heated above the temperature of the oil.

The still a, Fig 59 is of box-like form and of a capacity corresponding to a horizontally disposed cylinder eight feet in diameter and eighteen to thirty feet in length. It is supported above a fireplace b for heating and has its upper portion exposed to the atmosphere with little or no protection against cooling. It is provided with a dome c. A burner d has a gas supply pipe e provided with a controlling valve f. The still, when its bottom becomes heated to incipient redness (the ordinary indication of danger to a still bottom from overheating should distillation be continued), should be able to withstand an internal pressure in such excess of eighty pounds per square inch above atmospheric pressure as to afford a proper margin of safety.

The intermediate section of the still (see Fig. 60) is best protected both from the atmosphere and from the fire gases, the contents of the so protected portion being not less than about half the capacity of the still. As shown, about a third
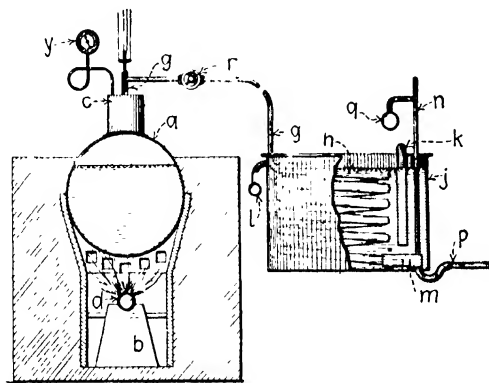
Fig. 59. — Chamberlain cracking process, sectional view.

of the exterior surface of the still is exposed to the atmosphere, approximately another third is exposed to the fire gases, and the remaining portion, approximately one-sixth on each side, is inclosed by and in contact with the walls of the still setting. The vapor pipe g leads from dome c to a condenser coil h immersed in a tank j. Water is supplied to tank j by pipe k and withdrawn therefrom by pipe l. At m within tank j is a gas separating box with a gas escape pipe n leading from its top and a distillate outlet pipe p leading from the bottom to a receiver (not shown). At q is a gas main for carrying away the gas to be burned.

The vapor pipe g is provided with an expansion valve r. As the best conduct of the pressure distillation, Chamberlain observes, requires a close regulation of the volume of escaping vapors, the valve port s, Fig 61, is of small size as compared with the bore of vapor pipe g, which bore should not be less than about three inches in diameter in order to avoid difficulty from choking. The valve shown is of the needle type. Heretofore in plans for distilling petroleum oils under superatmospheric pressure a relief valve which rises automatically when the pressure reaches a certain degree and closes when the pressure falls below the same degree has been utilized. The use of such automatic valve is not necessarily excluded; but its use is stated to be attended with no advantage; while, on the other hand, it adds com-

plication to the apparatus and is liable to cause danger or inconvenience by stick-
ing. If used, it would be advantageous to provide means for manually regulating
the extent of the valve's opening and for forcing it positively to and from its seat,
should occasion arise

The still is provided with a pressure gage y, a safety valve for relieving said
pressure should it accidentally become excessive, a pyrometer to indicate the
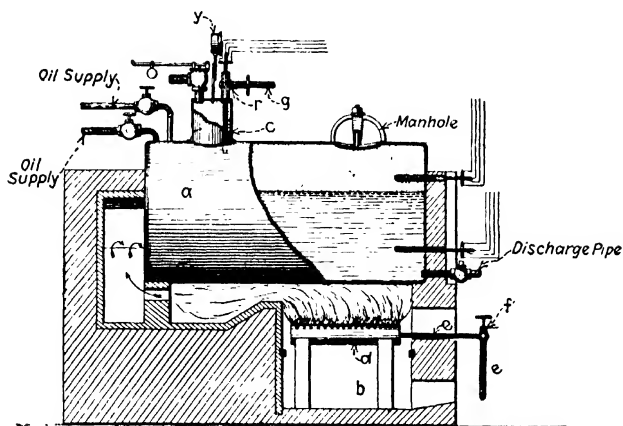
Fig. 60. — Chamberlain cracking process, side view.

temperature of the oil in distillation, a second pyrometer to show the temperature
in the vapor space at the front of the still, a third pyrometer to ascertain the

Fig. 61. — Pressure control valve
(Chamberlain process).

temperature of the vapors as they leave
the dome c and pass over to be condensed
as distillate, an oil supply pipe, a valved
discharge pipe for the residual product,
a steam pipe for introducing steam at the
close of each run in order to expel hydro-
carbon vapors and to cool the still off more
rapidly, and a manhole for cleaning out
the still at the end of each run. For ob-
taining the oil to be supplied to still a
crude petroleum is distilled to dryness
under atmospheric pressure in externally
heated stills. After the collection of the
water white burning oil (kerosene) distillate
and of such amount of the mixed distillate
coming over subsequently as may be de-
sired, the distillate which is subsequently
received is collected in the receiver for
heavy paraffin distillate as long as it is
sufficiently free from still wax to be readily
pressed for paraffin wax. Assuming that the crude oil operated upon is from
the Kansas oil fields and has itself a specific gravity of 0.863, this collection may

well include all the distillate which at the condenser outlet is between 0.855 and
0.904 in specific gravity at 60° F. (15 6° C.). Distillate which is received after-
ward in the distillation of the crude oil may also be distilled to dryness, and the so
obtained distillate, so long as it is free from still wax, be added to the heavy paraffin
distillate of the crude oil run. The material obtained in this way may be treated
with sulphuric acid and alkali in the manner customary for treating heavy paraffin
distillate preparatory to chilling and pressing. So treated, and with its content of
paraffin wax intact, it constitutes heavy paraffin distillate in the form considered
best to employ for decomposition in the still a. This material consists principally
of hydrocarbons, which (if separate) would be liquid at 60° F.; but it also contains
over four per cent by volume of paraffin wax (in solution). Its liquid portion com-
prises hydrocarbons with viscosities normal to medium grades of lubricants (from
one hundred and seventy seconds to two hundred and ninety-seven seconds, as
defined above) and also hydrocarbons with viscosities normal to heavy grades of
lubricants (from two hundred and ninety-seven seconds upward) as well as hydro-
carbons whose viscosities lie between those normal to kerosene and those normal
to medium lubricants (between seventy seconds and one hundred and seventy
seconds). Each of these species of liquid hydrocarbons is present in above 10
per cent by volume.

A sample from a particular lot of treated and unpressed heavy paraffin dis-
tillate which, Chamberlin reports had as a whole a specific gravity of 0.881 at 60° F.
was chilled and pressed for paraffin wax and yielded the latter at the rate of six-
teen and a half pounds to each 42-gallon barrel of the unpressed distillate (equiva-
lent to six per cent by volume). The pressed sample was then reduced with free
superheated steam introduced into the oil and with fractional condensation of
vapors in a series of condensers at different temperatures in the manner customary
in obtaining lubricating oils (light and medium grades as distillates and heavy
grades as residues) from pressed paraffin distillate and in this reduction yielded
(1) distillate with viscosities at the condenser outlet up to seventy seconds equal
to one per cent by volume of the unpressed distillate, (2) distillate with viscosities
at the condenser outlet between seventy seconds and one hundred and seventy
seconds equal to approximately fifty-six per cent, and (3) distillate with viscosities
at the condenser outlet between one hundred and seventy seconds and two hundred
and ninety-seven seconds equal to approximately fourteen per cent, leaving (4) re-
sidual oil equal to approximately twenty per cent. There was thus an estimated
loss of about two per cent by volume in the assay. The treated and unpressed
heavy paraffin distillate is introduced into the still a until the latter is six-tenths
full. The contents of the still are then gradually raised in temperature, with valve
r open, until the air has been expelled from the still and oil appears as condensate
at the condenser outlet. Next the valve r is closed and the pressure in the still a
is allowed to accumulate until the gage y shows 75 pounds per square inch above
atmospheric pressure. Then the valve r is cautiously opened; and the heating
is carefully regulated to maintain a pressure of 75 pounds without greatly exceeding
it. The extent to which the valve r is opened is an important matter. It may
well be opened so that distillate is received from the condenser h at the rate of about
two per cent by volume of the original charge per hour of running. The valve r
can be adjusted if considered necessary, but in normal running the valve opening
may be constantly established, so as to allow a continuous escape of the vapors
through it; and it need not be altered in size, thus allowing an approximately uni-
form escape of vapors with an approximately uniform pressure in the still. As
distillation proceeds, the oil in distillation becomes gradually hotter. Its tem-

peratures will be higher than those of the oil in a parallel run under atmospheric pressure; but they may be (and in distilling heavy paraffin distillates under a pressure of seventy five pounds have been found to be) below those at which the vapor tension of the undecomposed oil is *estimated* to equal the still pressure on the basis of considering the rise in vapor tension of the undecomposed oil for a given number of degrees F. above its boiling point to be equal (or sufficiently nearly equal) to the rise in vapor tension of benzene (coal tar naphtha, C_6H_6) for an equal number of degrees F. above its boiling point; and considering the temperatures of the oil in distillation in a parallel run under atmospheric pressures to represent the boiling points of the undecomposed oil. A table is given below which shows the temperatures of the oil in parallel runs on heavy paraffin distillate under atmospheric pressure and under seventy-five pounds superatmospheric respectively; and it will be observed by reference to it that at corresponding periods of the runs the difference is less than 131° F.; which is the difference in temperature between benzene at its boiling point (where its vapor tension equals the pressure of the atmosphere) and at the point where its vapor tension is seventy-five pounds to the square inch above atmospheric pressure.

The evolved vapors are cooled in the exposed upper part of still *a* and in dome *c* to a considerable extent (say between about 150° F. and about 350° F. below the contemporaneous temperatures of the oil in distillation) before they pass over

Fractions 5 % each	Atmospheric pressure				75 pounds gage pressure			
	Liquid oil, degrees F	Vapors in dome, degrees F.	Specific gravity	Time, minutes	Liquid oil, degrees F.	Vapors in dome, degrees F.	Specific gravity	Time, minutes
1	663	588	.8236	40	766	512	.7669	48
2	679	582	.8473	43	756	520	.7673	43
3	691	624	.8529	45	763	525	.7682	46
4	701	635	.8586	38	769	530	.7762	35
5	710	635	.8581	40	775	529	.7770	37
6	715	658	.8540	43	778	530	.7758	41
7	722	656	.8571	41	777	535	.7809	38
8	734	676	.8560	40	782	540	.7818	41
9	740	680	.8555	44	793	545	.7844	46
10	741	635	.8473	43	804	550	.7945	37
11	752	655	.8519	40	811	554	.7967	38
12 .. '	760	688	.8514	38	815	546	.8053	36
13	765	691	.8524	39	834	550	.8170	40
14 . ..	770	696	.8534	45	842	546	.8299	50

Total distillate 70 %; time 9 h. 39 m ; total dis. 70 %; time 9 h. 36 m.

Percentages in table by weight, not volume; total distillate 72 % by volume in run under atmospheric pressure, and 78.2 % by volume in run under 75 pounds gage pressure.

to be condensed as distillate. Such cooling results in a partial condensation of vapors and the formation of condensate which returns to the oil in distillation. It is thought that some hydrocarbon components of the oil in still *a* will vaporize without decomposition, owing to the presence in the still *a* of the vapors of lighter (more volatile) hydrocarbons formed by decomposition, notwithstanding the fact that the temperature of the oil in distillation is below the estimated boiling point of the latter under the pressure in the still *a*.

The preceding table gives figures which were obtained in runs performed at the rates indicated in the table with a small still (a horizontal cylinder 20 inches in diameter by 42 inches long with a dome four inches in diameter and six inches high) on batches from the same lot of oil, one under atmospheric pressure and the other under a superatmospheric pressure as near 75 pounds to the square inch as practicable. The total hours and minutes of performing the respective runs, in connection with the total percentages received, show average yields of distillate equal to about seven and a half per cent by volume of the original charge per hour in one run and about eight per cent per hour in the other; but in industrial operations a lower rate is considered better.

The specific gravities in the table are those of the several fractions of distillate of 5 % each by weight, and the times in minutes are those in which the fractions were severally received.

It is considered best in distilling under pressure that the evolved vapors should not be heated above the temperatures of the oil in distillation. As shown, therefore, only the bottom third of the exterior surface of the still is exposed to the fire gases; so that the walls of the vapor space, even when this space is enlarged by progress of the distillation, will not be exposed to the fire gases. The cooling of the vapors is effected by the exposure of the still top and dome to the atmosphere. The work performed by the vapors in expanding as they pass the valve *r* in distillation under high pressure, with this valve within a short distance from dome *c* also exerts a cooling effect on the vapors in the dome *c*. The condensate as formed drops (or else runs down the sides of the still) into the oil in distillation. A partial condenser connected with the still by a vapor pipe and a run back for returning condensate could be used instead of or in addition to cooling in the vapor space (including dome space when a dome is used). By having the middle section of the still inclosed by and in contact with the walls of the still setting, the vapors are protected not only against overheating, as just mentioned, but also against the undue cooling which might result from enlargement of the vapor space during the run, were the middle section exposed to the atmosphere. The distillation is continued as long as it is safe to do so, in view of the superatmospheric pressure in the still. The limit of safety is about reached when the appearance of the still bottom indicates incipient redness. The run being terminated, the asphaltic material in the still *a* is withdrawn into a receiver; the still is subsequently cooled (after introduction of free steam to expel the vapors, the manhole being opened as the steam first enters); the still is cleaned; and it is then ready to receive a new charge of the treated *unpressed* heavy paraffin distillate.

The high pressure distillate from condenser coil *h* may be collected in a single receiver and then fractionated into naphtha, burning oil (kerosene) and a heavier oil useful as gas or fuel oil. This heavier oil, also any residue obtained in rerunning the burning oil (kerosene) portion of the high pressure distillate, could be added in whole or in part to a new charge of the heavy paraffin, distilled if desired. Other oils could also be added, such as residues (bottoms) from rerunning the water white distillate and the mixed distillate of the crude oil run. In-

stead ot a single condenser *h* as shown, a series of condensers maintained at different temperatures could be applied to the pressure still *a*.

The asphaltic residual material withdrawn from the still *a* at the close of the high pressure run in which the figures of the table were obtained had as a whole a specific gravity of 1.0772, and was as a whole about ninety-eight per cent soluble in carbon bisulphide and about eighty-two per cent soluble in naphtha obtained from Kansas crude oil and consisting of hydrocarbons with specific gravities ranging from 0.7526 to 0.7692. If desired, the pressure distillation can be stopped before the material in the still attains the specific gravity mentioned. Also, further distillation can be carried on under atmospheric or reduced pressure. As obtained from the high pressure still the asphaltic material will ordinarily be soft and sticky even at 0° F, on account of maintaining the distillation only while it can be carried on with safety; but by reduction (partial evaporation) under atmospheric pressure at appropriately high temperature and with introduction of superheated steam into the melted material, it can be brought to such condition that when cool a lump can be molded and drawn out into threads. Distillate obtained from a reduction like this can be added to heavy paraffin distillate to be distilled under the high pressure mentioned; it could be used as gas oil or fuel oil.

The solution of the asphaltic material as obtained from the high pressure still in the naphtha mentioned (in such proportions as to give the desired fluidity for application) constitutes a varnish or protective coating. The material can be dissolved in this way and used after reduction and oxidation. While it is considered best to charge the pressure still with an oil which represents an entire range of hydrocarbons from and including some with the intermediate viscosities mentioned (70–170 seconds Engler) to and including those recovered from heavy paraffin slop, more or less of these hydrocarbons can be collected separately, if so preferred, and only the remainder of them charged into the still.

Oil containing liquid hydrocarbons with viscosities normal for medium and heavy lubricating oils and oil containing hydrocarbons with the intermediate viscosities mentioned (70–170 seconds Engler) can be distilled separately under pressure and the resulting products can then be mixed. In this way burning oil (kerosene) from distilling oil of the latter kind under pressure can be improved by the better quality of that from distilling oil of the former kind. Larger yields, however, both of naphtha and of burning oil (kerosene) have been obtained, it is stated, from distilling mixtures of (1) hydrocarbons with viscosities normal to heavy lubricating oils and (2) hydrocarbons with the intermediate viscosities mentioned, than from distilling like volumes of the two kinds of liquid hydrocarbons separately; and the same principle would hold true with respect to mixtures containing hydrocarbons with viscosities normal to medium lubricating oils. Better results are attainable, it is believed, by distilling oil in which two or more of the three kinds of liquid hydrocarbons mentioned are naturally present than by separating these hydrocarbons and then forming a mixture artificially of them in their original proportions.

In making heavy paraffin distillate a certain amount of decomposition is considered necessary in order to form crystallizable paraffin wax. It is provoked by introducing little or no superheated steam into the still and by cooling the evolved vapors sufficiently to form a condensate which is returned to the oil in distillation. The cracking customary in making heavy paraffin distillate is considered advantageous where this distillate is to be subjected to pressure distillation, for one reason because it removes from the distillate certain coke forming elements; and, if preferred, it can be carried further in preparing distillate for subsequent pressure distillation than is customary in preparing heavy paraffin distillate.

In the pressure distillation it is considered best, as mentioned above, to use about 75 pounds to the square inch above atmospheric pressure. Above this pressure the yields of naphtha and burning oil have not been found to increase (rather the reverse); while, of course, the danger increases with the pressure. Below 75 pounds pressure the yields have been found, it is stated, to fall off gradually with the diminution of pressure; so that under 30 pounds the yield of naphtha has been about three-fifths and under 20 pounds less than half of the yield under 75 pounds; while the yield of burning oil (kerosene) under 30 pounds has been about four-fifths and under 20 pounds less than three-fourths of the yield under 75 pounds. In order that, in a run under 30 pounds, the temperatures of the oil in distillation may not be as high as those at which the vapor tension of the undecomposed oil is estimated to equal the still pressure, these temperatures should not be so much as about 73° F. above the temperatures attained at corresponding periods in a parallel run under atmospheric pressure. In runs under a pressure other than 30 pounds and 75 pounds, the temperatures of the oil in distillation should be within a corresponding maximum above the so attained temperatures in order that they may be less than those at which the vapor tension of the undecomposed oil is estimated to equal the still pressure. The vapor tensions of benzene (C_6H_6) are known for a wide range of temperatures. Such tension amounts to 30 pounds superatmospheric at about 73° F. above the boiling points (about 250° F.), the boiling point of benzene being about 177° F. (80° C.).

There may be petroleum, it is said, which does not yield paraffin wax, but which does yield distillate composed of liquid hydrocarbons divisible by their respective viscosities into the three kinds mentioned; and there may well be petroleum which does not yield distillate having hydrocarbons so divisible. All crude petroleum can be distilled to dryness under a suitably low pressure, in order to obtain distillate to be decomposed by distillation under high pressure, which distillate may contain at least the higher boiling hydrocarbons down to but excluding last runnings that would be objectionable on account of the presence of still wax or other heavy matters of sticky character, but not necessarily excluding desirable hydrocarbons recoverable by the re-running of slops. Working on the continuous system (in which a more or less continuous stream of oil is supplied to a high pressure still and a like stream of residuum withdrawn during the progess of the distillation) is permissible; although it is considered more advantageous to work by the batch system.

C. P. Dubbs [1] arranges a number of vertical stills in series (Fig. 62) as A^1, A^2, A^3, etc. The residue from distillation under cracking conditions (pressure) in still A^1 passes into A^2 and is redistilled at higher temperatures than prevailed in A^1. This operation is extended to a number of stills (A^1–A^6, Fig. 62). Heat is supplied to the oil by means of steam coils within the still (see Fig. 63). In other words, oil flows through all the stills in the series, from A^1 to A^6.

Before reaching still A^1, the fresh oil flows through the reflux condensers R^1, R^2, etc., in the direction of the arrows drawn in full, heavy lines (Fig. 62). (These arrows are numbered, in order to facilitate following the course of the liquid oil, whereas the course taken by the vapors is shown by arrows drawn in broken lines.) The oil, therefore,

[1] J. S. C. I. 1917, 921 U. S. Patent 1,231,509, June 26, 1917.
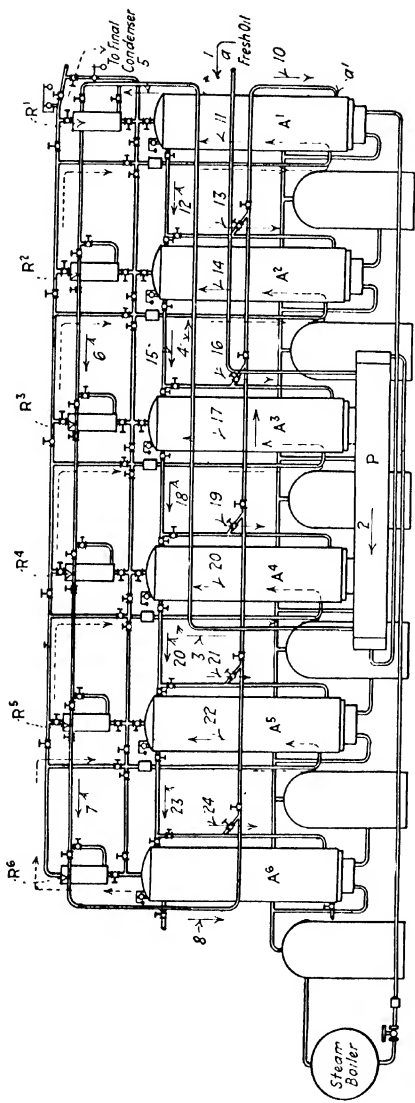
Fig. 62. — Assembly of continuous pressure stills with heat exchangers, proposed by C. P. Dubbs. [Solid arrows (numbered) show path followed by oil; arrows in broken lines indicate course of vapors.]

is the medium which cools the vapors in the reflux condensers, which, therefore, act as heat interchangers. The oil also passes through the steam heated preheater P (Fig. 62), on its way to still A^1. The vapors produced are forced to pass back through the series of stills and through the oil in the stills, in a direction counter to the flow of liquid oil. What evidently takes place is that the oil residues are redistilled at successively increasing temperatures, while the vapors produced are very thoroughly scrubbed at suc-

cessively decreasing temperatures. Heat economy and thorough separation appear, therefore, to be some of the main objects in view. The gasoline finally obtained should be free from any heavier oils, owing to the scrubbing which the vapors receive.

The temperature is reported to vary from a minimum of $200°-500°$ F. ($93°-260°$ C.) to a maximum of $500°-2000°$ F. ($260°-1090°$ C.), and the pressure varies from a minimum of 50 pounds per sq. in. to a maximum of 1000 pounds per sq. in. The material in passing through the apparatus forms a pool in each still and is subjected in the various stills to a progressively increasing temperature while the vapors and gases given off have not only been made to percolate up through the liquid and caused to mix with the liquid but have also been caused to travel in the reverse direction from the liquid so as to be subjected to progressively decreasing temperatures. This arrangement permits the vapors and gases to be subjected to comparatively high

Fig. 63. — Detail of steam-heated pressure still. C. P. Dubbs

and low temperatures without excessive pressure, while the vapors in their final form, as they pass to the condenser, have been scrubbed through the liquid and their temperature greatly reduced so that as they pass from the still A^1 to the condenser, they are at a relatively low temperature to that to which they have been subjected in the still A^6. This treatment tends to prevent any heavy vapors from passing to the condenser since the stepdown in temperature, as the vapors and gases pass through the various stills toward the condenser, tends to condense any heavy vapors and cause them to be carried back with the residuum and again subjected to the higher temperature. Also the vapors and gases being reduced in temperature by percolating through the liquid in the successive stills having lower temperatures, the heat units which are extracted in cooling the vapors and gases are transmitted to the liquid which is traveling in the reverse direction and is increasing in temperature.

Roy Cross [1] heats a body of oil to a high temperature under very high pressure to effect cracking. The vaporous products are allowed to expand into contact with a mass of untreated oil. This is said to be an improved method of separating the heavier from the lighter products of the cracking operation, and at the same time aids in preheating the untreated oil.

In a number of the methods advocated for the transformation of heavy hydrocarbons into light hydrocarbons with simultaneous distillation, on account of the high temperature required, there is an undesirable quantity of heavy hydrocarbons carried over in the vapor form and these must be separated from the light hydrocarbons by a subsequent treatment. When, in order to prevent their distillation, the vapors of the heavy hydrocarbons are passed into a condenser cooled sufficiently to allow only the light hydrocarbons to pass through, there is an abstraction of a large amount of heat which retards very much the rate of transforma-
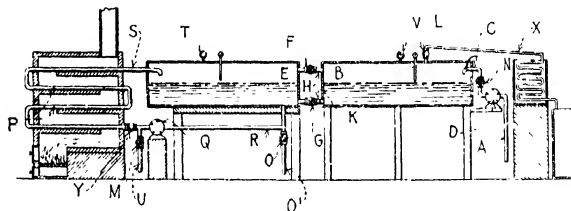
Fig. 64 — Type of pressure still proposed by Roy Cross.

tion of the heavy hydrocarbons as well as very greatly increases the total amount of heat required for the treatment. By the method described, the heavy hydrocarbon vapors do not pass from the container since they are readily condensed and absorbed by the cooler incoming hydrocarbons not yet under treatment and the incoming hydrocarbons are sufficiently heated to lessen the time of treatment required to later transform them into light hydrocarbons.

Heavy petroleum oil is introduced from a supply line A, Fig. 64, into the container B through a pipe C by means of a pump D until the containers B and E are half full, the valves F and G in the connecting pipes H and K being open. Then the pump D is stopped, the valves L, F, G, M, N and O are closed and heat is applied to the pipes P carrying the oil to and from container E which acts as a vapor container and exit and not as a container for a bulk of supply oil. The oil is made to circulate by means of the pump Q through pipe R into pipes P in the furnace and back into container E through inlet pipe S. Then a pressure of 600 pounds per square inch is allowed to develop as shown by gage T and a temperature of between 300° C. and 450° C. (572°–842° F.). The actual operation as to pressure and temperature will vary, depending upon the character of the heavy hydrocarbons under treatment and upon the end boiling point of the product desired. Valve F is now opened slowly allowing the pressure to gradually develop in container B, being fully open when the pressure in B is equal to the pressure in E. Valve L is now opened but not sufficiently to allow any considerable change in pressure or temperature in container E. When the temperature of the oil in B tends to exceed

[1] U. S. Patent 1,255,138, Feb. 5, 1918.

the end boiling point of the light hydrocarbons desired, pump Q is started, and cold oil is introduced through pipe C with valve N open until the temperature is reduced to the proper point. Valve M in pipe C may be opened, valve Y closed and pump Q operated to remove sludge as frequently as required by the accumulation of semi-solid matter With proper regulation the treatment goes on continuously without operation of valves, the body of heavy oil in B being kept at such a temperature that light hydrocarbons of a desired volatility go forward to the condenser while heavier hydrocarbons are taken up in the heavy oil and returned to the heating zone. There is a continuous feed of heavy oils to and through the system with withdrawal of light vapors The vapors pass only in one direction from container E to and through B and the liquids pass only in the one direction through B toward and into E. The heat of the vapors of heavy oils produced in E is taken up by the oil in B.

The vapors of the light hydrocarbons pass through the pipe X into a condenser which is connected to a gasoline reservoir To avoid blowing out oil sludge through the pump Q valve O in pipe O' may be opened to clear the carbon from container E while valves F and G are closed

Prevost Hubbard [1] describes a process which may be applied to fuel oil, that is reduced crude oil, which consists in subjecting the oil to high temperature and pressure for a relatively short period of time in a vessel in which the oil exists, during the operation, both in the liquid and in the vapor state, for example fifteen minutes. At the end of the digesting process the liquid oil may be drawn off, cooled and distilled to recover light naphtha while the vapors formed during the operation are cooled to condense light hydrocarbons. One of the advantages of this method, according to Hubbard, is that the oil residue after the removal of light hydrocarbons therefrom yields an oil which is as suitable for fuel as the original charge.

In **Curran's** process,[2] a battery of stills with a common feed pipe discharge through individual valved pipes into a common drum in which light and heavy distillates are separated. Connected with the drum is a condenser for light hydrocarbon vapors. The heavy distillate passes by gravity from the drum to a separate still which is connected to the same condenser. Steam is passed into all the stills.

J. W. Court [3] cracks oil in a still under more than 50 pounds pressure, the vapors are condensed under a similar pressure, and the high boiling fractions are returned to the still where relatively cool steam is introduced and the mixture is maintained under a pressure of one atmosphere in a main condenser.

In the fractional or destructive distillation of hydrocarbon oils, the pressure in the still is raised and lowered alternately according to

[1] United States Patent 1,326,056, Dec. 23, 1919.
[2] J. S. C I. 1918, 200A; U. S. Patent, 1,255,714, Feb. 5, 1918.
[3] Chem. Abs. 1918, 2438; Canadian Patent 184,279, May 14, 1918.

a method of **C. Turner.**[1] The still is closed to raise the pressure and is
opened to lower the pressure rapidly solely by expansion of the vapors.
The operation is effected without intermittent cooling, except such as
may occur during the lowering of the pressure. Pressure steam is
blown into the oil until the pressure reaches five pounds per square
inch. The vapor outlet is then opened until the pressure falls to two
pounds, whereupon the vapor outlet is closed and steam is again ad-
mitted. The operation is continued until the steam, which is of twenty
pounds pressure, no longer effects distillation; after this stage, super-
heated steam is used.

The Palmer Process

Palmer[2] increases the yield of volatile hydrocarbons from petroleum
residues, by digesting them under pressure of the evolved vapor (60-
400 pounds per sq. in.) at a temperature above 200° C. (392° F.) but
below that at which carbonization takes place, and without the ad-
dition of steam, the heating being continued until the greater portion
of the residue is converted into more volatile compounds, which are
separated when the pressure is relieved.[3]

The process consists, further,

(1) In the complete separation of the so-called " cracking " from the distilling,
the former being carried out at high pressure, usually in excess of four atmospheres,
while the latter is conducted at or below atmospheric pressure.

(2) In conducting the " cracking " in heavily constructed digesters capable
of withstanding enormous pressures, while supplying sufficient heat to liquefy,
to volatilize, to create pressure, to furnish latent heat of volatilization, and to fur-
nish *the requisite endothermic heat of formation.*

(3) In utilizing the pressure to control the reaction, the greater the pressure
the greater will be the decomposition, recomposition and polymerization. The
pressure is controlled in each case by the equilibrium established and varies accord-
ing to the materials treated, the resulting products, and the factors of heat and time
of action but ordinarily pressure reaching 130 pounds is sufficient to effect the
necessary conversion.

(4) The time of action. This usually, aside from the time required for the pre-
liminary melting and heating in the reservoir, occupies but a very few minutes.

In carrying out the process the residues, substantially non-volatile below 300° C.;
(572° F.) such as " Florence," " Boulder," " Wyoming," " California " and " Loui-
siana " pitches or residues, are first introduced into a steam jacketed reservoir

[1] J. S. C. I. 1915, 1004; Chem. Abs. 1919, 659; U. S. Patent 1,151,422, Aug.
24, 1915; British Patent 120,584, Nov. 23, 1917.

[2] **Lomax, Dunstan** and **Thole,** J. Inst. Petrol. Tech. 1916 (3), 36-120; U. S.
Patent 1,187,380, June 13, 1916.

[3] It is important to note that this process is said to be applicable to heavy
residues and is not limited to " gas oils " as raw material. It is essentially a
decomposing and not a distilling process. Moreover the time of treatment as given
is exceptionally short.

in which they are melted, and are then introduced into a high pressure digester. In Fig. 66, A is a tank or reservoir provided with a cover, steam-jacket, drainage pipe, and steam inlet pipe. An outlet pipe, provided with a valve, is connected with a digester B. The digester, which is constructed of half-inch steel, is provided with cap, a manhole, and pipe extensions. A jacket with steam coils completely surrounds the digester. The pipe-extensions C and D project through the jacket and are provided with a check valve and a stop-cock respectively. These extensions are connected to a still.

The residues treated consisted, in so far as could be determined from the specific gravity and melting points, of mixtures of hydrocarbons of the paraffin series C_nH_{2n+2} of the range $C_{20}H_{42}$ to $C_{28}H_{58}$. These residues are empirically known as
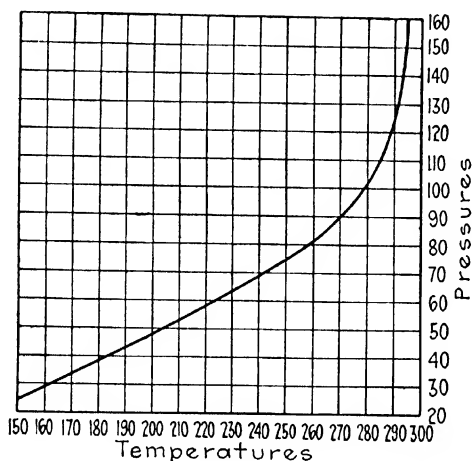
Fig. 65.

residues or pitches from, for example, "Florence," "Wyoming," "California," and "Louisiana" pitches, which were the ones actually tested and operated on by this process.

During the treatment in the digester, B, which usually did not exceed a few minutes, the pressures gradually increased with the temperature, according to the curve shown in Fig. 65, until a pressure of 130 pounds was reached, when there was apparently a sudden conversion of the materials present into more volatile compounds which, it was observed, caused *a rapid increase in the pressures without the indication of any great increase in temperature.* Since the heat was being uniformly applied, it is apparent that at this pressure there was a large absorption of heat, which prevented any noticeable indication of an increase in temperature. This absorption of heat was evidently due to the formation of new compounds which, as the results show, are to a certain extent, at least, cyclic in character. In order that the pressure may be accurately controlled during the operation, the check valve E may be adjusted for any degree of pressure desired. Upon an increase of the pressure above that to which the valve is set, the vapors from the digester will pass over into the still F. Steam coils are utilized because of the accuracy with which the temperature can be

adjusted, particularly, if superheated steam is employed. The volatile products obtained from the above treatment were drawn off through the pipe G and, collected in a still and subjected to distillation separately from the undecomposed residues remaining in the digester, at atmospheric pressure and upon fractional distillation, gave results as follows: Up to 100° C. (212° F.) about 5 per cent distillate; between 100° C. (212° F.) and 150° C. (302° F.) about 10 per cent to 20 per cent distillate; between 150° C. and 200° C. (302°–392° F.) about 10 per cent to 20 per cent distillate; between 200° C. and 250° C. (392°–482° F.) about 20 per cent to 30 per cent distillate; between 250° C. and 300° C. (482°–572° F.) about 10 per cent distillate.

While the first fraction doubtless contained some volatile paraffin C_nH_{2n+2}, the higher distillates were mixtures of some paraffins, some aromatic bodies, and, it is said, considerable naphthenes or " cyclic " or " closed ring " paraffins, such for example as polymethylenes, C_6H_{12}, and their homologues. The materials which had been previously non-volatile below 300° C. (572° F) after treatment uniformly yielded from 65 per cent to 75 per cent of volatile matter at temperatures varying from 100° C. to 300° C. (212°–572° F.). Moreover, when the residues of one treatment were mixed with the residues of another batch, and were again treated there was no accumulation of non-volatile residue. In fact a non-volatile residue remaining from the last fraction of one treatment even if subsequently treated alone, would often be decomposed in a manner similar to that of untreated residues when heated alone since each treatment would have its quota of undecomposed residue according to the equilibrium established. Accordingly, each residue when retreated would decompose exactly as though it had not been previously treated, as decomposition takes place at the appropriate equilibrium and long before all the residue is transformed.

In Fig. 65 the curve shown illustrates the process when operating up to 300° C. (752° F.) and the pressures ranging from 30 pounds up to 160 pounds, and experiments show, according to Palmer, that when operating even up to 400 pounds, the decomposition, recomposition and polymerization, other things being equal, are directly dependent upon the increase of pressure, and that the radical transformation into many new compounds having new molecular arrangements, does not begin much below five or six atmospheres independent of the temperature. On the other hand, the experiments indicate, it is stated, that at pressures ranging from 20 to 30 atmospheres the formation of new compounds takes place with great rapidity. In all cases the volatile products of decomposition increase with more pressure at temperatures from 200° to 300° C. This indicates it is not merely the high temperature, but rather moderate temperature and high pressure that govern the decomposition and determine the result.

As an example: When operating with heavy, waxy, tarry or pitchy materials, such as " Florence," " Boulder," " Wyoming," " California " and " Louisiana " pitches, at temperatures ranging from 200° to 325° C. (392°–617° F.) and under pressures of from 60 to 90 pounds, but a relatively small percentage approximating from 25 per cent to 35 per cent of volatile products were obtained. With temperatures from 200° up to 325° C. (392°–617° F.) and pressures ranging from 100

to 150 pounds to the square inch, a large percentage of the originally non-volatile material treated was transformed into volatile compounds, the percentage ranging from 50 per cent to 75 per cent of the original. At pressures ranging from 150 pounds up to 300 and 400 pounds per square inch, and at temperatures of from 200° to 325° C. (392–617° F.) from 75 per cent to 90 per cent of the materials were converted into volatile products. These products were in all cases subjected to distillation, at or below atmospheric pressure, separately from the digesting operation.
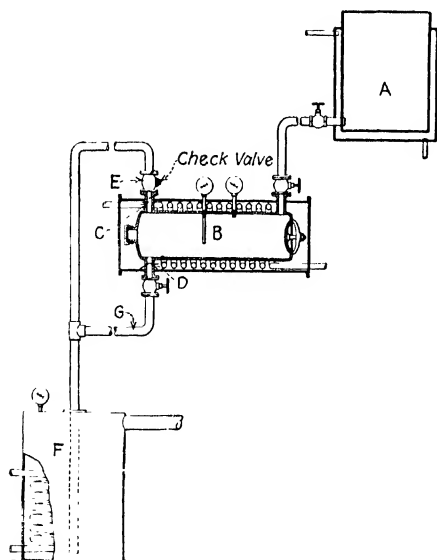
Fig. 66. — Palmer process.

The effect of high pressure during cracking in producing "saturated" low boiling hydrocarbons appears to be well demonstrated by **Snelling.** His method consists in digesting heavy, high-boiling hydrocarbons under high pressure, until certain equilibria are apparently reached.[1]

If we write the equations

(1) $C_{20}H_{42} = C_{15}H_{30} + C_5H_{10} + H_2$

(2) $C_5H_{10} + H_2 = C_5H_{12}$

(3) $C_{15}H_{30} + H_2 = C_{15}H_{32}$
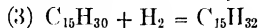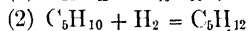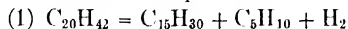
[1] In endeavoring to explain complicated reactions, there is little difficulty in presenting equations on paper which seemingly elucidate the phenomena in question but which may correspond in nowise to the actual changes. A very free use of the imagination has been made by some writers in this field. The authors offer the above merely as an illustration or suggestion of the possible character of one of the reactions that may occur in cracking at high temperatures and pressures.

and *if we assume* that the temperatures employed are such that reaction (3) goes only to a slight extent, and also that a reversal of reaction (1) is not favored and that conditions are favorable for reaction, (2) then it follows that by allowing the system to come to equilibrium at that temperature under which the above assumed conditions obtain, the final result would be the sum of reactions (1) and (2) namely, the formation of pentadecene and pentane from decadecane.

Polymerization also may be a factor in producing saturated bodies. For example, two molecules of butylene could combine to produce a cyclic compound.

$$2(CH_3 - CH = CH - CH_3) = \begin{array}{c} CH_3 - CH - CH - CH_3 \\ | \quad | \\ CH_3 - CH - CH - CH_3 \end{array}$$
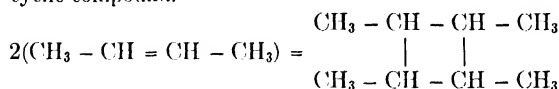
Or, dissimilar unsaturated hydrocarbons may combine, for example, ethylene and amylene.

$$C_2H_4 + C_5H_{10} = \begin{array}{c} CH_3 - CH - CH - CH_2 - CH_3 \\ | \quad | \\ CH_2 - CH_2 \end{array}$$
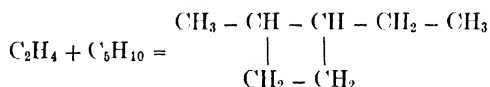
The processes of Palmer and Snelling are apparently based on attempts to cause some of the reactions to come to equilibrium at high temperatures. **Bergius** and **Billwiller** [1] employ a similar method, hydrogen being added to the system initially. The gasoline produced by these methods seems to possess a particularly high percentage of saturated hydrocarbons.

W. O. Snelling [2] converts low grade crude oils, asphaltic oils, paraffin wax, "rod wax," kerosene, lubricating oils, fuel oils, tarry still residues, etc., into a product resembling high grade Oklahoma crude oil by heating in a closed vessel to such a temperature that the vapors evolved produce a pressure of 600–800 pounds per square inch. The volume of oil is from one-fifth to one-half of the cubic capacity of the container. The presence of catalysts (deflocculated graphite, colloidal carbon, colloidal nickel, etc.) may facilitate the operation, but it is said not to be essential. The average amount of gasoline (distilling up to 150° C.) found in the "artificial crudes" produced in this way is 10 to 20 per cent, with 20 to 40 per cent burning oil. These yields may be increased, it is said, by distilling off the lighter oils and treating the residue again, and the process may be worked continuously by providing means for removing the vapors produced.

[1] See chapter on the use of reducing gases.
[2] J. S. C. I. 1915, 1045, 267; Chem. Abs. 1916, 388; British Patent 18,419, Aug. 7, 1914; Int. Conv. Nov. 11, 1913.

It is said that during the digesting operation " excess " carbon is formed and deposited as mud. Gas is also formed which does not condense after the reaction vessel is allowed to cool.

The following example of the method used (on a laboratory scale) is given.[1]

Three hundred cubic centimeters of a solid white paraffin, melting point 50°, specific gravity 0.925, was used. This was sealed in a vessel of 1100 cubic centimeters capacity and heated until a pressure of 800 pounds was indicated, then cooled The pressure of the residual gas was 130 pounds. The product was a heavy liquid resembling Pennsylvania crude oil, dark green by reflected light, dark red-brown by transmitted light. Its volume was 305 cubic centimeters, specific gravity 0.770 and the gasoline yield on distilling to 150° was 48 cubic centimeters or 16 per cent. By removing the gasoline and repeating the process he has obtained from paraffin 70 per cent of water white gasoline, the remaining 30 per cent representing the gas formed, and some free carbon.[2]

The Iroline Company[3] employing Snelling's method, obtain low-boiling hydrocarbons suitable as fuel for internal combustion engines by heating liquid or fusible hydrocarbons of higher boiling point in a closed vessel to a temperature sufficient to develop a pressure of 200–500 lbs per sq in , the volume of oil being from 0.125 to 0.5 that of the vessel The liquid is withdrawn under sufficient pressure to retain the low-boiling hydrocarbons in solution at a lower temperature and these are recovered by distillation[4]

Trotter[5] decomposes kerosene by distillation under pressure. Previous to this treatment the kerosene is subjected to the action of superheated naphtha vapors. When, as a result of pressure distillation, the gravity of the residue falls below 58° Bé superheated gasoline vapors and steam are injected into the residue to maintain the requisite relations between temperature and pressure.

Apparently the idea is to maintain pressure during the cracking process at a high practical value while still keeping the temperature of the residue relatively low The low-boiling products from the initial cracking treatment are successively redistilled at increasing temperatures and decreasing pressures. It is claimed that kerosene can be largely converted into light naphtha by Trotter's method.

A recent suggestion by **L. McOmber**[6] relating to distillation and condensation under pressure is of interest McOmber employs a tube still with the customary run back, radiator, water condenser and receiving tank. In addition to these, a pump is interposed between the radiator and water condenser by which means pressure in the condenser can be regulated independently of the pressure in the still; for example distillation may be conducted under 75 pounds pressure while condensation may be effected under as much as 200 pounds pressure or more. This procedure is claimed to result in a large yield of light naphtha.

[1] Bull. Am Inst. Mining Eng 1915, 695–704.
[2] See also **Snelling**, French Patent 180,899, Oct 4, 1916.
[3] See Marks, British Patent 3327, Mar. 2, 1915; J. S. C. I. 1916, 828.
[4] See also British Patent 18,419 (1914) and J. S. C. I. 1915, 1045.
[5] U. S. Patent 1,339,727, May 11, 1920.
[6] U. S. Patent 1,345,452, July 6, 1920.

CHAPTER VIII

DISTILLATION UNDER PRESSURE — *Continued*

Development and Use of Tube Stills and Devices to Obtain Smooth Operating Conditions

The development of tube stills for decomposing or cracking oil recalls the evolution of the water tube steam boiler. The conditions which make a water tube boiler more serviceable than shell boiler also render tube oil stills[1] superior in some respects to the older shell stills; and once the pressure distillation of gas oil to produce gas naphtha attained commercial proportions, refiners soon saw the advantage of using tube stills for this purpose.

E. M. Clark[2] uses a combination of still and cracking tubes which is shown in Fig. 67. *A* is an upright shell having a rounded bottom, from above which leads a pipe containing a force pump *B* of any suitable construction. This pipe leads from the discharge side of the pump to one end of a coil *C* in a furnace. The opposite end of the coil communicates with the shell *A* at its upper end, from which leads a discharge pipe to the upper end of a water cooled condenser coil *D*, the discharge end of which, containing a valve, leads to a receiving drum for the distillate. A tail gas pipe rises from the lowermost branch of the coil through the condenser tank, above which the pipe contains a valve *E*.

The apparatus shown is particularly designed for the manufacture of gasoline by distilling under pressure the residue of petroleum distillation, such as fuel oil The liquid material to be distilled is charged into the reservoir, which may contain several thousand gallons. With the pump in action and the furnace going, the contents of the shell are circulated, passing through the pump, which forces the liquid through the coil *C* from which it returns in heated condition to the reservoir *A*. By continuing this circulation, the heated liquid returning from the coil to the reservoir heats the contents of the latter and the resultant vapors pass into the condenser. The vapors build up a pressure on the contents of the reservoir of from about 3 to 7 atmospheres and raise their temperature to about 650° F. (342° C.) and as the run proceeds, to about 850° F. (455° C.). Gases accumulating in the condenser are allowed to escape from time to time, on opening the valve *E*, thus relieving the gas-pressure, which is liable to accumulate in the coil and obstruct the action of the apparatus. From time to time the valve *F* is opened for discharg-

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[1] For pressure distillations.   [2] U. S. Patent 1,119,496, December 1, 1914

ing the distillate into the drum. This distillate is crude gasoline and may be subjected to further treatment. Carbon is formed in the liquid passing through the coil *C* but the liquid is circulated so rapidly that accumulation of carbon in the coil is said to be prevented.[1]

In tube stills or tube cracking processes the formation and deposition of carbon has been a *bête noire* and recent developments have shown that with high velocity of travel of the oil or vapors through the tubes, a scouring action is established which more or less effectively maintains the tubes unobstructed by carbon.

W. Anderson and **J. Meikle** [2] distill heavy oil (creosote oil, blast-furnace oil) under pressure in a specially constructed still consisting of
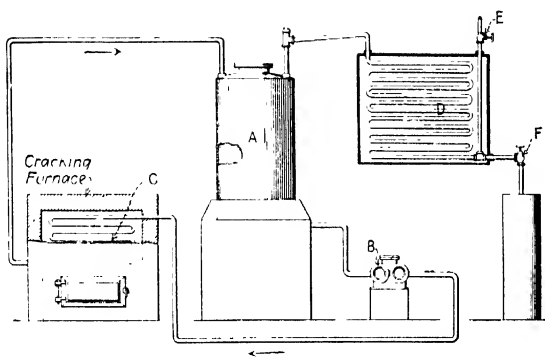
Fig. 67. — The Clark tube still.

two superposed drums separated by a combustion chamber, the lower drum, or both drums, being traversed by fire tubes. The two drums are connected by a downcomer and return tubes, the oils being fed into the upper drum by a pipe coaxial with the downcomer. The distillate is mixed with steam, and the mixed vapors passed through a superheater and then through a condenser.

S. H. Edwards [3] prefers to carry on cracking, to a fractional extent only, rather than to push the process as far as it will go. By employing the apparatus shown in Figs. 68, 69 and 70, it is stated that practically continuous cracking takes place.

Within certain limits, it may be noted, the lower boiling point fractions of the oils usually treated by pressure distillation are more easily cracked, thermolyzed or converted into low boiling point hydrocarbons at the pressures and temperatures

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[1] See also E. M. Clark, Chem. Abs. 1916, 1929; British Patent 1421, Jan. 28, 1915.

[2] J. S. C. I. 1917, 1001; British Patent 108,508, Aug. 4, 1916.

[3] U. S. Patent 1,170,884, Feb. 8, 1916.

usually employed than the higher boiling point fractions of the oil to be treated. It
is asserted that by carrying on the process to a fractional extent by extending the
operation only to the degree of having cracked principally those lower boiling point
constituents of the oil being treated which are most easily converted, the process is
economical and efficient, leaving as a residue a product suitable for use as a gas or
fuel oil without further processing.

The still consists of a nest of heating tubes A^1 (Fig. 68). The still also includes
an upper drum A, which is partitioned by transverse diaphragms c (Fig. 70), so
as to present compartments which are connected in circuit with groups of tubes.
A lower drum B (Fig. 68) is also provided and partitioned by diaphragms like the
upper drum, the compartments of the lower drum being connected with the lower
or rear ends of the groups of tubes. The still thus consists of a number of sections,
made up of a group of tubes and the connected drum compartments. The still is
thus divided into a number of small circulating units, bringing the oil into rapid
and repeated contact with the heating surface of the tubes, and allowing the vapor
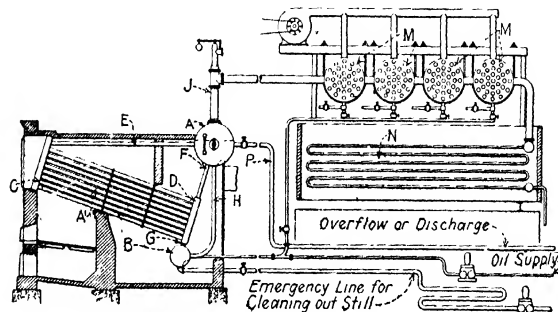
Fig. 68. — Tube still according to S. H. Edwards.

formed in each circulating unit to become disengaged from the liquid in the upper
drum. The sections are connected in such manner that while the oil being treated
is circulating continuously through the tubes of the various sections and giving up
its vaporized portions in the upper drum, a progressive circulation of the oil as resi-
due, less the vaporized portion, takes place from one section to another, successively.
The partitions of the upper and lower drums are similarly placed, and corresponding
upper and lower compartments are connected with the ends of the same sets of tubes.
The communication between sections is through the diaphragms in the drums.
(See Fig. 70.) The upper drum is disposed transversely, partly inside and partly
outside the rear and upper portion of the setting. The lower drum is placed trans-
versely within the lower rear portion of the setting. The tubes are connected in
tiers with sectional headers C and D (Fig. 68), the upper ends of which are connected
by tubes E and F with the upper drum. The lower drum is connected with the lower
ends of the headers by short tubes G. In addition, in order to insure an adequate
supply of oil to the heating tubes A^1, the lower, or rear, ends are connected with the
upper drum by downcomers H. The latter open into the rear side of the lower
drum, and are two in number for each pair of upper and lower drum compartments,
and of the same size as the tubes F The connections between the drum compart-
ments are formed by openings a and b (Fig. 69) through the diaphragms near but

somewhat above the bottoms, in order to guard against their becoming choked by deposits. These openings are comparatively restricted in order that part of the oil in each section may be caused to circulate repeatedly in it before passing to the next section, or, in other words, to render the progress from section to section comparatively slow. However, the action may be varied by making the area of communication for the oil between compartments larger or smaller. The openings also perform the function of equalizing the level of the liquid in the several sections to guard against any of the sections going dry.

The diaphragms of the lower drum usually extend all the way to the top of it, being closed with the exception of the openings *b* (Fig. 69). The diaphragms of the upper drum, on the contrary, terminate some distance below the top of this drum, so as to leave a common vapor space in the upper part. From the top of this space there leads a vapor line *J*, which may carry a safety valve. The supply line *K* (Fig. 68), for raw oil or distillate to be redistilled, enters the lower drum, at the compartment at one end of it. This compartment, the drum compartment above and the connected group of heating tubes constitute the first section As shown in Fig. 70, the first section may be wider than the last section, including more of the heating tubes The residue discharge line (not shown) leads from the upper drum

Fig. 69.

compartment of the last section. Its inlet end is inside the drum, a short distance above the bottom, and may extend upward and thence bend laterally, passing through the wall of the drum at such height that the liquid level determined by the height of overflow is below the tops of the diaphragms in order that communication for the oil between compartments is confined to the openings *a*, Fig 69 A pump in the supply line delivers the oil to the still.
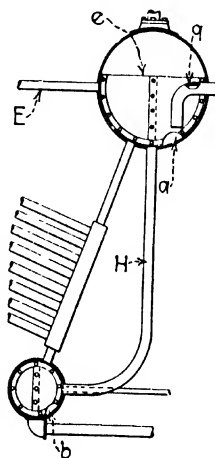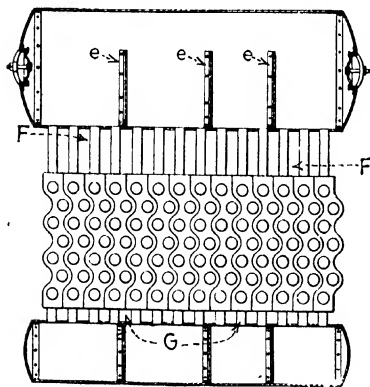
The vapor line conducts the vapors to the first of a series of aerial condensers (*M*, Fig. 68), which comprise a row of horizontal drums having air tubes passing through them. Air is supplied to these tubes by an air line having a blower so that the cooling effect is definitely controllable. The vapor line enters the side of the first condenser drum, the interior of which around the cooling tubes is filled with

Fig. 70.

the vapors when the still is in operation. The highest boiling point fractions condense here and settle in the bottom of the drum, which thus constitutes its own collector. From the opposite side of the first drum the vapors still uncondensed pass to the second drum by a short tube and so on through the drums in series, fractions of successively lower boiling point being condensed in the several drums.

From the last drum the remaining vapors pass to a water condenser (N, Fig. 68) from which crude gasoline may be drawn off from time to time. If the operation being conducted is the thermolyzing of high boiling point fractions having boiling points of upward of 400° F. (204° C.) (gas oil, etc.) for the purpose of producing gasoline, the aerial condensers should be so proportioned as to return all of the oil fractions coming over with the vapors having higher boiling points than the desired naphtha-containing distillate, which, alone, is condensed in the water condenser Each of the aerial condensers has an individual outlet from its bottom, and all these outlets may enter a common return line which joins the supply line and thus reaches the lower drum of the still, entering the first compartment.

The overflow line (P, Fig. 68), through which the residue escapes from the still may lead to storage, or may lead into or constitute the supply line of a second still. While it is possible to build one still with sufficient circulating units to carry on the process to any desired degree of concentration of the residue, it is not advisable for
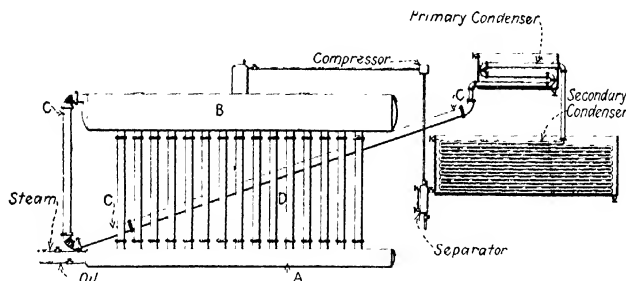
Fig. 71. — Pressure still proposed by Rowsey.

practical reasons to carry the still beyond a certain size, preferably not more than twenty tubes wide, because of mechanical limitations which may be encountered If it is desired to carry the process beyond the degree of concentration attainable in one still the liquid residue in the last compartment of the upper transverse drum of the first still may be led to the first section of the lower drum of a second still, and the process carried on from that point in a way entirely similar to that in the first still except that, due to the heavier concentration and the higher average boiling points of the material composing that residue, higher temperatures will naturally prevail. The process may be carried in a third and even a fourth still, to a point where the degree of concentration is too great to admit of further practical continuous processing of the residue. A vent opening q is formed in the top of the overflow line, at a point within the drum. The function of this vent is to prevent the possibility of a siphoning action being set up, thereby creating a tendency to lower the level of the oil below the point fixed by the position of the overflow or discharge line P.

Rowsey [1] combines a horizontal cylindrical drum (B, Fig. 71) with two similar lower drums A. The lower stills A are in the same horizontal plane and are connected to the upper drum or manifold B by means of " risers " D. The apparatus also includes a primary reflux

[1] J. S. C. I. 1917, 999; U. S. Patent 1,235,384, July 31, 1917.

condenser as well as a final or secondary condenser. The long vapor outlet pipe also constitutes a part of the cracking equipment since it is maintained at or above cracking temperatures.

The vapors of distillation pass from the top manifold of the still into the distillate conducting pipe C, following the course of this pipe first in a downwardly direction and then in an upwardly inclined direction to the primary condenser coil. In the primary condenser the unconverted and partially converted vapors that will condense into hydrocarbons of high boiling points are condensed and returned by reverse flow from the primary condenser into the distillate conducting pipe C maintained at or above oil cracking temperatures and, as a consequence, the condensed vapors delivered back are revaporized and cracked to be returned to the primary condenser in the form of hydrocarbons of lower boiling points, which will pass to the secondary condenser and thereafter be collected in the separator.

The permanent gases, or incondensable vapors, pass through both of the condensers and into a separator and these gases are forced into the dome of the upper manifold of the still. The permanent gases are thereby retained and due to their retention the formation of such gases is claimed to be retarded, this effect being obtained on the supposition that if sufficient permanent gases are present in the apparatus an equilibrium will occur after which no further permanent gases will be produced. During operation a pressure of from 30 to 200 pounds is maintained in the apparatus, this pressure varying according to the nature of the oil being treated and the amount of steam introduced into the apparatus. The temperature maintained in the upper manifold of the still may vary from 700° to 1200° F. (371°–649°C.).

By the admission of steam into the still, decomposition of the oil is retarded in order to crack the oil mildly, converting it into a distillate of from 48° to 50° Baumé gravity, and of low boiling point. The oil treated may be of any nature from light fuel oil to heavy residuum and the extent of the cracking is regulated by the pressure and temperature maintained and the amount of steam introduced into the apparatus. It is claimed that by the use of steam a distillate which contains a high percentage of hydrocarbons of the paraffin series is obtained.

Herber[1] proposes to rotate the whole still, instead of circulating the oil in a stationary still. The still (Fig. 72) is a horizontal shell, provided with hollow trunnions, concentric with the axis of the still. These trunnions constitute the vapor exit pipes. Holes in the trunnions register with the lower end of stationary vapor pipes. The process

[1] U. S. Patents 1,227,558 and 1,227,559, May 22, 1917.

is evidently designed to be continuous. Oil is fed into the still by feed pipes which extend horizontally through the hollow trunnions. The weight of the still is carried partly by the bearings which support the trunnions, partly by a series of rollers beneath the still. Distillation and condensation may be conducted under pressure.

Sherman [1] states that very efficient cracking of high boiling oils can be effected at a relatively low temperature if the period of heating is correspondingly prolonged. He uses cracking tubes in conjunction with a still, as shown in Fig. 73. The features of this apparatus are a pres-
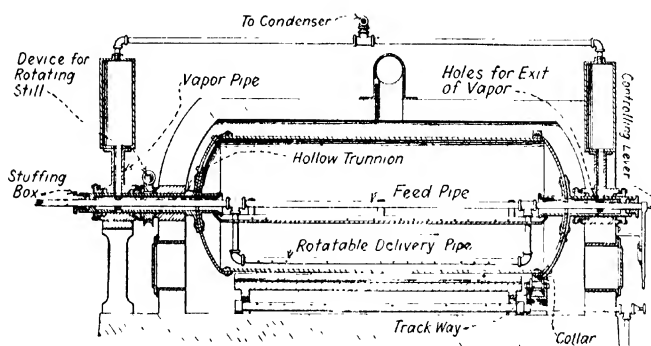
Fig. 72. — Rotating still, according to Herber.

sure still A, a reflux condenser B, a carbon filter C and a false bottom of fused metal F in the still A. The cracking tubes D are also jacketed with fused metal. The average range of cracking temperature is from 675° to 750° F. (357°–399° C.) and the first 35 per cent of a batch of oil should be converted, it is said, into low boiling fractions of a gravity of 58°–63° Bé., at temperatures not exceeding 715° F. (380° C.). The temperature of the body of oil in the still during this period may run between 650° F. and 700° F. (343°–371° C.). The oil which is cracked in the tubes comes both from the still, direct through the carbon filter C, and also from the reflux condenser. The light oil vapors produced in the cracking coils D pass on their way to the reflux condenser, through the pipe E into the main vapor space of the still.

The reflux condenser allows only oils of the desired gravity to escape, and returns the higher boiling portions to the cracking tubes where they are mixed with oil which comes direct from the still through the filtering device C. The low temperatures employed, the presence of the fused metal heat conveyor, the constant movement of oil from the still

[1] U. S. Patents 968,088, August 23, 1910; and 1,288,711, Dec. 24, 1918.

to the cracking tubes through the carbon filter — these are features which are intended at least partly to overcome the difficulty presented by the deposit of carbonaceous matter.[1]

An unusual type of still for the production of lighter hydrocarbons from gas oil, crude oil, kerosene or other hydrocarbon oils has been developed by **F. A. Kormann.**[2]   He fills most of the space within a still or conversion chamber with solid porous absorbent material such as porous brick formed by burning a mixture of shale clay, bone and willow charcoal.   Before the oil is introduced, this mass of porous material is
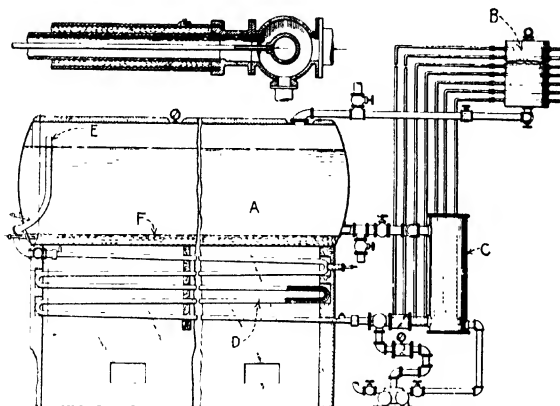
Fig. 73. — Tube still, with indirect heating proposed by Sherman.

heated to expand its pores and rarefy their gaseous content.   Oil to be treated is supplied to the conversion chamber, is taken up by the porous material (which, if in the form of bricks, contracts), and is subsequently distilled off with steam, with the obtainment of a large increase of light hydrocarbons over the amount originally present in the treated oil.   The absorbent material is supposed to be used repeatedly without vitiation by carbon.   The theory is advanced by Kormann that production of light hydrocarbons may be the result of pressure upon the oil entrapped within pores of the absorbent material.   By employment of this process, it is stated that 16 per cent of gasoline was obtained from a Mexican crude oil naturally containing only 2 per cent gasoline and in treating kerosene of 44.5° Bé practically complete conversion to a liquid of 52° Bé. is claimed by Kormann to be effected.

[1] See also Sherman U. S. Patent 1,260,584, Mar. 26, 1918.
[2] Chem. Abs. 1920, 1215; U. S. Patent 1,332,849, March 2, 1920.

Special Devices for Removing Carbon. Other Safety Methods

Born [1] lays chains on the bottom of the still. This is said to prevent a hard cake of carbon from baking on to the bottom.

It is stated that in commercially practising the Dewar and Redwood process on a large scale, in which the capacity of the still and the quantity of the material treated is several hundred barrels, it is found that the accumulation of carbon on the still bottom precludes continuing the run long enough to convert into lighter hydrocarbons more than about one-fourth of the material contained in the still. This is because the carbon formed in the process is a good non-conductor and the still bottom under it becomes hot and, if the run were continued, would soon burn through the bottom of the still as well as retard the distillation itself. In
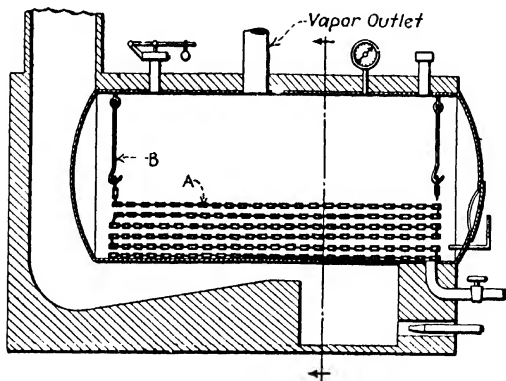
Fig. 74. — Born's proposal for overcoming difficulties of carbon deposit.

order to overcome this difficulty a chain A, or series of chains, is provided lying along the bottom and along the curved sides of the still, Fig. 74, and covering approximately one-fourth of the total circumference. The chain may be either one continuous line, looped at the ends and the ends suspended free from the bottom by means of hooks B to enable the chain to be more easily removed, or it may have a number of individual sections. In operation the liquid contents are heated to their boiling point by the heat from the furnace and circulate freely about and around the length of chain. The carbon which is produced by the breaking up or cracking of the charge under the action of the heat, instead of depositing on the still bottom proper and causing the objectionable circumstances referred to above, forms, for the greater part, on the chains lying on the bottom of the still. After the run has been completed, or whenever the accumulation of carbon renders it necessary, the still is opened, the ends of the chain are removed from the hooks and the chain is pulled out of the still. In this way, most of the carbon adhering to the chain is removed with it, and the small amount adhering to the still bottom has been so broken up that such deposits can, it is stated, very readily be removed.

[1] U. S. Patent 1,234,124, July 24, 1917.

Another proposal for continuously removing carbon deposit has been advanced by **Setzler.**[1]

The still *A*, Fig. 75, is equipped with a rotating shaft *B*, mounted in water-cooled stuffing boxes *C*, and fitted with a pulley wheel *D*. Inside the still, there is attached to the shaft, a helicoidal cleaner *E*, of such diameter and length as to engage the entire heated inner periphery of the still. At the front and rear ends of the shaft respectively are water pipes *F* entering passages drilled in the ends of the shaft *D*, a distance equal at least to the length of the shaft inside of the stuffing boxes. A discharge pipe is attached to the still at its bottom, near the rear end.

Ordinarily such a pressure still is charged approximately to one-half its capacity with gas oil and power is turned on the motor connected with gear wheel *D*, which revolves the helicoidal scraper or cleaner inside the still. The still is heated so that the temperature of the contained oil rapidly rises, until it has reached about 700° F. (371° C.) at which temperature the pressure begins to rise. By the time pressure has reached 100 pounds, the temperature will have risen to approximately
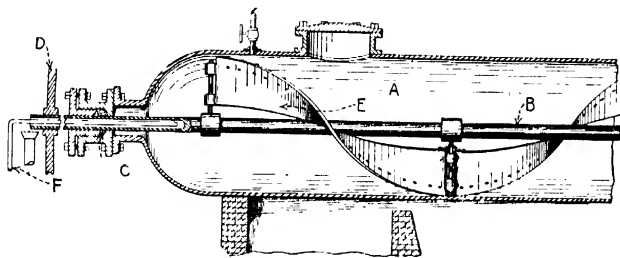
Fig. 75. — Still, with scraper advocated by Setzler

730° F. (388° C.), at which temperature and pressure carbon begins to split off from the heated hydrocarbons. These have boiling points of 80° to 350° F. (27°–177° C.) and a Baumé gravity of 56 to 58.

It has been found that without the use of suitable cleaning, scraping or scouring, that carbon, at the instant it is freed from its previous combination, being of amorphous character, and settling out of the mass of gas oil, seems to be attracted or drawn to the heated bottom still sheets. Normally, these particles of carbon growing together and agglomerating over the bottom sheet, form a coating of carbon, of "semicrystalline" form, which would have dangerous results. By using a helicoid cleaner, continuously revolving inside the still, the carbon which has been freed from its combination is kept in an amorphous condition, and suspended throughout the mass of oil. Any carbon which becomes attached to the bottom is promptly removed. It is also stated that with a still working under the conditions of pressure and heat necessary to effect pressure distillation of hydrocarbons, precautions must be observed for maintaining the hermetic seal of the still. The vulnerable points of the still described exist in the shaft entering the still at its longitudinal axis. This shaft must have an extremely effective packing maintained at all times, within the stuffing boxes, in order to prevent excessive leakage, yet the packing would be subjected normally to such high temperatures as would rapidly deterio-

[1] U. S. Patent, 1,292,966, Jan. 28, 1919.

rate the packing material. *To avoid this, there is used the simple water-cooling method* found in the terminally bored shaft *B,* which entering the stuffing boxes at either end is maintained in relatively cool condition at all times, by the internal flow of water.

After the operation described has progressed, until approximately 10 per cent of the volume of gas oil charged into the still has been converted into other products boiling between 80° to 350° F. (27°–177° C.) and the Baumé gravity of the products is found to range from 56 to 58, gas oil is continuously pumped into the still at the front end, at the same time that the new products referred to are conducted off through the vapor line. Having established the quantity entering and leaving the still, the operation is continued until approximately
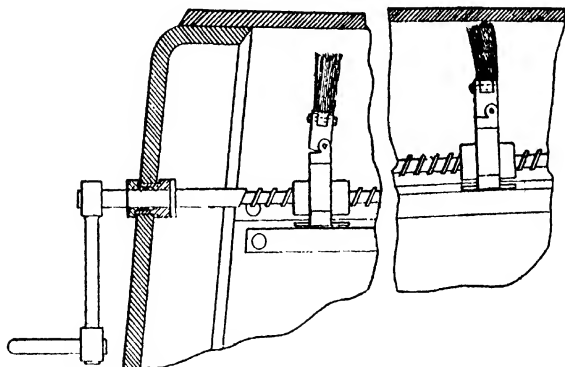
Fig. 76. — Ragosin's proposal for removing carbon by means of rotating brushes.

50 per cent of the volume has been conducted off, when the oil in the still will have reached approximately 24° Baumé. The contents are then either continuously or periodically drawn off.

The liquid, condensed and collected, may be distilled in the ordinary manner, primarily for its gasoline content, while the heavier distillates may be reintroduced into the still for further treatment after the carbon has been allowed to settle out.

Ragosin [1] passes oil vapors from a still through a cracking chamber in which the vapors are superheated. A rotating brush device is used to remove carbon deposit (see Fig. 76).

A. D. Smith, [2] using a combination of still and tubes, provides the still with several rotating steel brushes which aid in keeping the bottom of the still free from carbon deposit. In addition to this, portions of

[1] British Patent 1411, Jan. 18, 1898.
[2] U. S. Patent 1,239,423, Sept. 4, 1917.

the charge are periodically pumped through filters to remove gum-yielding constituents.

He cracks fuel oil, gas oil or distillates of paraffin nature at a pressure of 125 to 150 pounds and at a temperature of 600° to 700° F. (316°–371° C.). A rapid circulation is maintained during the process so that the objectionable carbon deposition on the heating surfaces of the still is greatly reduced and the yield of crude gasoline increased, according to Smith, 70 to 80 per cent due to ability to prolong the process by removing danger of burning out the heated metal surfaces. The removal of this carbon is said to be attained by sweeping at intervals portions of the charge to interchangeable filters and returning the carbon-free fluid to the still together with
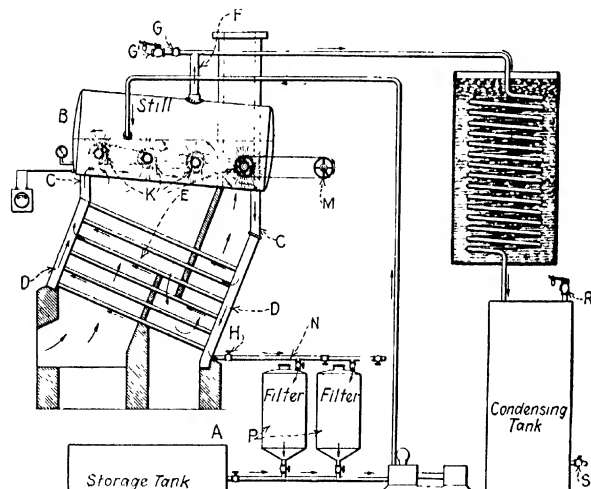
Fig. 77. — Tube still, with rotating brushes, proposed by A. D. Smith.

fresh distillate, the action being thus rendered continuous, a most essential feature is regards increasing the output from a given size of apparatus. By carbon-free fluid is meant a liquid from which suspended carbon particles likely to deposit on heated metallic surfaces have been removed.

It has been noted that, however desirable is the method of applying pressure throughout the course of distillation while vapors are undergoing condensation, nevertheless a certain constant loss takes place through evaporation of the lighter gasolines passing from the liquid to gaseous state as the condensate flows from the end of the condensing coil to the receiving tank where it passes from high pressure to atmospheric pressure. This loss may be reduced from forty to fifty per cent, it is stated, by keeping not only the vapors themselves under pressure while undergoing condensation, but the liquid condensate as well, relieving pressure in excess of 150 pounds only at the storage tank. The latter is allowed to nearly fill before removal of contents, and the condensate is blended with low gravity naphtha, thus entraining and fixing lighter portions of condensate produced under pressure so that subsequent evaporation is reduced to a minimum.

In Fig. 77, the gas oil, fuel oil or paraffin residue is charged from a storage tank A by a pump, through a pipe line to a still. The still consists of the shell B which is mounted in a setting over a furnace with its longitudinal axis at a slight downward inclination from front to back. Nipples or connections C open into the bottom of the shell at its front and back ends and these nipples are connected to the tube boxes or headers D which are arranged at the front and back ends of the furnace chamber. A series of parallel tubes E connect the headers, and the tubes and headers are arranged at a considerable upward inclination from back to front below the shell in the path of the hot gases from the furnace. The outlet F is provided with a vacuum valve G and safety valve G'. A vapor line leads from the outlet to the condenser. An outlet pipe for residuum leads from the lower end of the back header, and is normally closed by a valve H. Within the boiler shell are arranged a series of revolving brushes K, which may be made of steel wire or other metal capable of withstanding heat and corrosion. The brushes are connected together with driving chains arranged within the shell and the rear brush is mounted on a shaft which passes through a stuffing box in the side of the shell and is provided with a pulley on its outer end. The pulley is belted to a pulley on the line shaft M, enabling the series of brushes to be rotated. The brushes are rotated in the direction shown by the arrows, thereby assisting in maintaining the circulation in the still, and also sweeping the bottom of the shell free from carbon. The shell B has a large capacity in proportion to the capacity of the tubes.

As the suspended carbon accumulates, a portion of the liquid contents of the shell is withdrawn at intervals, for instance every thirty minutes, through the residuum outlet N to the filter P, where it is passed through fuller's earth or spent bone char and is freed from carbon. The filters are readily removable for the purpose of cleaning.

The vapors are condensed and fall into a condensing tank. The same pressure is maintained in the condensing tank as throughout the remainder of the system. Any excess of pressure above 150 pounds on the system is relieved by the relief valve R. When the condensing tank is nearly full, its contents may be withdrawn through the valve S and mixed immediately with low gravity naphtha, thus fixing the lighter hydrocarbons.

According to a process by **A. F. Bell** [1] the carbon deposit is removed by means of scrapers and carbon collecting devices mounted on the hollow shaft of an inclined, mechanically rotated still.

In Fig. 78, A is the still set at an inclination. The still has a hollow central shaft B which is mounted on trunnions C for rotation, by means of power transmitted through a gear D. The oil is supplied to the still by means of a pump E,

[1] U. S. Patent 1,231,695, July 3, 1917.

the outlet pipe from which communicates with the oil feed pipe *F* which enters the hollow shaft of the still. The oil then enters the still through holes in the central shaft. The distilled vapors enter the central shaft and pass from it into the vapor outlet *H*. A pipe *K* returns to the oil feed pipe *F* such portion of the vapors as are not cracked. A small part of the fresh oil is used to lubricate the stuffing box at *M*.

S′, S′ are scrapers. These extend along the length of the still at its lowermost portion, and in contact with its wall. The scrapers are independent of each other, and each is provided with two arms *N* which are hung at *P* upon a shaft *R* common to all. The shaft *R* is carried in the lower ends of ring hangers *S* which at intervals are journaled freely in suitable bearings *T* on the central shaft *B*. Thus,
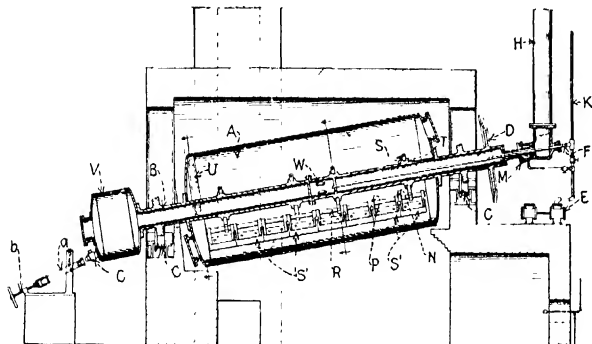
Fig. 78. — Rotating still, with scrapers suggested by A. F. Bell.

though the still and its central shaft rotate, the scrapers hang free and act upon the inner surface of the still wall throughout its entire circumference as the wall rotates against them. Each scraper, being itself pivotally hung by its arms, has flexibility. The carbon removed by the scrapers is directed by them and by the inclination of the still, to the lower end. In order to remove the carbon there is secured to the still at its lower end a scoop pipe *U*, the outer open end of which lies in the circumference of the still, and its inner end opens into the hollow shaft *B*, so that at each revolution the scoop pipe picks up the carbon and delivers it to the shaft.

Secured to the shaft and communicating with it is the reservoir chamber *V* with a valved outlet. The operation of the still is as follows: — Oil is supplied by the pump to the still which is being rotated, through the feed pipe *F*, and hollow shaft *B*, a portion of the oil being used to lubricate the stuffing box *M*. The vapors pass out through the holes *H′* into the hollow shaft *B*, past the transverse web supporting the inner end of pipe *F*, and up through the vapor outlet *H* to its condenser

and distillate connections. As cracking takes place more or less carbon is constantly deposited on the surfaces, which is continuously scraped off, and delivered to the lower end of the still, where it is picked up by scoop pipe U which delivers it inside of the revolving shaft B, and from there it finds its way to the reservoir chamber V. When it is necessary to remove the carbon which has accumulated in reservoir chamber V, the still is stopped revolving for a few minutes and the flexible pipe a is forced up by the screw b, so that it makes a tight joint on valved outlet C. The valve of this outlet is then opened, and due to the pressure inside the still, all of the loose carbon is pushed out into pipe a for delivery to a receiving tank.

In the cracking oil, the precipitated carbon may be prevented from adhering to the walls of the retort according to **L. A. Dubbs,**[1] by the scouring action of a non-reactive abrasive material, which is mixed with the oil in a finely divided form. Sand is suitable.

Another method of keeping cracking tubes free of carbon is advanced by **Francis X. Govers.**[2] Means are provided in a continuous tube furnace for introducing balls, singly and at regulated intervals, into the path of flow of the material under treatment prior to its entrance into the heating zone and for removing the balls after passing through the heating zone. The material is forced through the tube. The use of the balls is claimed to result in keeping the tube free from deposits.

Cochran[3] distills oil under pressure in a revolving retort or still which contains metallic balls, somewhat after the manner of a ball mill. The balls are said to act as heat conductors and also as attrition agents, aiding in the prevention of hard crusts of carbon deposit. By using, for example, nickel balls, a certain amount of catalytic action is claimed to take place.

J. B. Edwards[4] describes a safety device for preventing fires arising from a break in the vapor line of pressure stills.

It is stated that when pressures up to and even greater than a hundred pounds are employed, the resulting fire hazard has led to the adoption of certain precautions to prevent burning out the bottoms of the stills and discharging their contents directly into the fire. Such provisions, however, are of no effect in the case of a break beyond the still, that is to say, in the vapor eduction or condensing system. This system, or a portion of it, is subject to the same high pressure condition as the still, and if a break occurs in this part of the apparatus an immediate outrush takes place through the intervening part of the system to the break, and thus to the atmosphere, where, the oil and vapors being at a temperature above the flash point, immediate combustion takes place.

[1] J. S. C. I. 1919, 941 A; Chem. Abs. 1920, 118; U. S. Patent 1,319,053, October 10, 1919.

[2] Chem. Abs. 1919, 1409 and 1637; U. S. Patent 1,297,833, Mar. 18, 1919; Canadian Patent 190,114, May 6, 1919.

[3] U. S. Patent 1,296,367, Mar. 4, 1919.

[4] U. S. Patent 1,277,884, Sept. 3, 1918.

In this way, not only the still initially affected but many others assembled in the same battery or vicinity may be destroyed   Such conflagrations have• occurred with sacrifice of life, as well as heavy property loss

In Fig. 79, *A* represents a petroleum still having a vapor outlet at the top and toward the rear, from which leads the upwardly inclined vapor pipe *B* of large diameter, having a vertical neck *D* secured in the outlet, and at its upper end delivering the vapors to a pipe *E* of smaller diameter which conducts them to the top of an aerial condenser *F*, whence the distillate passes to a cooler coil *G*, and then through running•line *H* to receiving drum *I*, from which the gasoline or other distillate is drawn off past a high pressure needle regulating valve *K* to running tank *J*. This valve *K*, together with a valve *L* governing the escape of fixed gases from the receiving drum, are set to create the desired back pressure of the vapors in the system. The inclined vapor pipe is for the purpose of condensing and returning all products heavier than the desired distillate, and is constructed of the proper length and with the proper condensing surface for this purpose.[1]
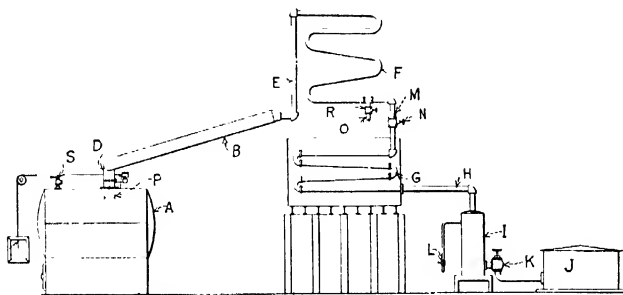
Fig. 79. — Modification of pressure still, by J. B. Edwards.

In this apparatus, which is representative of those now in use, there is no means, it is stated, which is capable of shutting off the flow through the eduction system, until the point *M* is reached, between the aerial condenser and the cooler coil, where a gate valve *N* is inserted.   This valve is not intended as a safety shut-off, and is indeed without practical value for such use, because the real danger of breakage lies in advance of this point.   This valve is merely to prevent the inferior distillate at the beginning of a run passing through and fouling the cooler coil, and then passing into the receiving drum and so on to the rest of the system, this early distillate being instead switched through a valve *R* to a branch *O*, from where it passes to a place of disposal.   Beyond these valves, that is to say, in the cooler coil and subsequently, the oil is below its flash point, but between them and the still the expansion strains are severe, and even with swing joints there is always the possibility of some part, from the neck *D* onward, giving way, in which case there is a forcible escape of highly inflammable

[1] See also chapter on Refinery Practice.

vapors and oil above the flash point, with the likelihood of the disas-
trous consequences indicated above.

To overcome this condition a safety shut-off is used, at the source, so that the
whole eduction and condensing system can be promptly cut off from the contents
of the still in case of a rupture at any point in the system.

A valve disk A, Figs. 80 and 81, is mounted for vertical movement within
the still to cooperate with a suitable seat b on the lower inwardly-projecting end of
the vapor neck D. This is suspended by a valve stem or rod C, the upper end of
which is pivoted loosely on a pintle d carried by the end of an arm e within the neck,
which arm in turn is mounted upon a rock-shaft f journaled in bearings g and h in
the neck. At one end this shaft passes through the wall of the neck, where a tight
joint is preserved by a stuffing box j, and with the outer portion of the shaft is con-
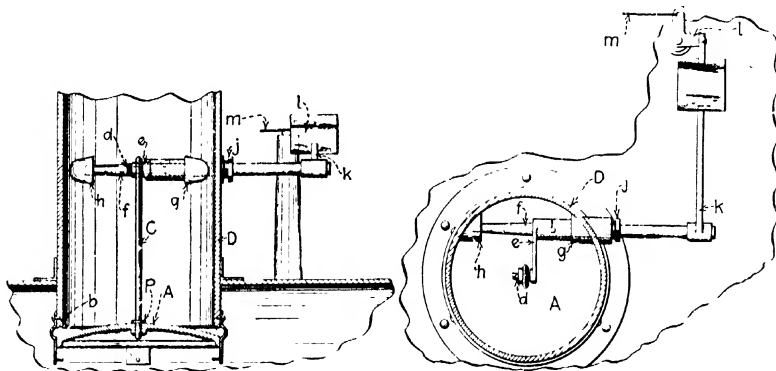
Fig. 80. — Safety device for pressure stills,   Fig 81. — Safety device for pressure stills, by
by J. B. Edwards (vertical sectional view).   J. B. Edwards (sectional plan view).

nected a weight arm k, which is normally sustained by a trigger l. A wire m passes
from this trigger to the front of the still and then down to a box, Fig. 79, located
at a convenient point and adapted to afford access to the end of the wire upon break-
ing a glass pane, after the manner of a fire-alarm box. In case of a break in the
eduction and condenser system it is the work of a moment to pull this wire, where-
upon the shut-off valve closes immediately and is held closed by the still pressure.
The counterweighting of the valve disk may be sufficient to counterbalance or to
overbalance the weight of this part.

W. B. Poole [1] proposes to obviate difficulties arising from carbon
deposits and to obtain higher yields of naphtha by employing a vertical
still enclosed in a heating flue in such a way that only the vertical
sides of the still receive direct heat. The bottom of the still projects
through brick work forming part of the heating flue. The lower portion
of the still which receives no direct heat acts as a receptacle or sump for
tarry matter and carbon.

[1] U. S. Patent 1,340,793, May 18, 1920.

A tall vapor pipe extends vertically through heating flues which may be fired independently of those which surround the still proper, so that products generated in the still may be subjected to higher temperatures in the eduction pipe.

Similarly a crude oil supply pipe is situated parallel and in proximity to the vapor eduction pipe with the result that the oil supply, on its way to the still, may be heated to a higher temperature than that of the oil in the still.

The Jenkins Process

In the Jenkins process, the observation is made that there is a zone between the surface of the oil and the top of the still where the temperature is much lower than in any other portion or zone of the oil or vapor, and that this is due to the absorption of heat by endothermic reactions. In this process, light vapors are removed from this "endothermic zone" by means of a special vapor collector, which is oil- or water-cooled and which also acts, therefore, as a reflux condenser. Hence, light vapors are removed from that particular zone where they are formed without allowing those vapors to be subjected to any superheating on their passage to the condenser. This process is claimed to produce larger yields of light naphtha (58° Bé.) than some other pressure still methods. It is also said to effect a corresponding reduction in the percentage of permanent gas formed.

The still and condensers are not in free communication (as in the Burton process), a pressure relief valve being situated in close proximity to the still, between the latter and a low-pressure air cooled expansion drum. It will be noted that a certain amount of condensation takes place under comparatively high pressure, but that this goes on *inside* instead of *outside* the still.

S. Schwartz,[1] working with the Jenkins process, concentrates his attention upon tapping off vaporous products of different densities from the vapor space by means of a vapor remover.

He states that where both liquid and vapor are present it is necessary to heat the body of heavy oil to between 550 and 1000 degrees Fahrenheit to produce the vapor pressure required to vaporize the heavy oil under the pressure required for cracking the heavy oil vapor to form gasoline or other light oils. If the vapor of the heavy oil is cooled below that temperature before any cracking obtains, condensation will occur. If, however, cracking has taken place the temperature of the vapor may be lowered without producing condensation, since the vapor pressure of the lighter oils is greater for any given temperature than it is for the heavier oils.

[1] J. S. C. I. 1918, 49A; Chem. Abs. 1918, 309; U. S. Patent 1,247,883, Nov. 27, 1917.

As noted above, it has been observed that close to the surface of the heavy oil in the still the temperature is usually lower than that of the oil below it or of the vapors and gases near the top of the still, which is possible since the vapor is largely cracked at that point. This drop in temperature close to the surface of the heavy oil suggests that an endothermic chemical action is taking place at that point and is attributed to cracking. The temperature difference is not constant in all cases but at a certain height above the surface of the heavy oil (in one apparatus employed this height was from one-third to one-quarter of the height of the top of the still above the level of the liquid) the temperature may be as much as 200 to 256 degrees Fahrenheit (111°–139° C.) lower than the temperature of the liquid oil. In this cool zone the percentage of fixed gases is very slight and if the vapor is withdrawn therefrom a larger yield of light oils is obtained than is otherwise the case. If the vapor is withdrawn from a higher part of the space above the heavy oil it is found to contain a higher percentage of permanent gases which are not desired. As the point of withdrawal is raised from the surface of the heavy oil to the top of the vaporizing chamber the density of the gases withdrawn decreases. This perhaps may be due in part to a progressive breaking up of the molecules of the vapor given off by the heavy oil, and in part to a stratification due to the different densities of the various gases, the ratio of the densities of methane (CH_4) and heptane vapor (C_7H_{16} — boiling point 98° C. (208.4° F)) for instance being about 1:6.

It is advantageous to produce artificially a still further reduction of temperature. This further reduction without reduction of pressure is claimed to increase the yield of gasoline and other light oils and to improve their quality. It has the further effect of first condensing, in part at least, any uncracked vapor or the vapor of oils having a higher boiling point than that desired, which may still remain in the cool zone so that these constituents will largely be returned in liquid drops to the main body of liquid for redistillation, and, second, checking, if not stopping, the further disintegration of the molecules of the light oils into permanent gases.

Thus, heavy oils on the one hand and permanent gases on the other hand are said to be largely eliminated from the cool zone. The result is to obtain a large yield of a product having a high percentage of hydrocarbons having boiling points between the most desirable limits, say 95° to 270° F. (35°–132.2° C.). Another advantage of this further reduction in temperature of the cool zone is that it enables the temperature of the liquid oil to be raised, without producing disadvantageous results, so that the production of vapor from the heavy oil and the subsequent cracking of that vapor are accelerated. The pressure is correspondingly raised, which also aids the cracking process. The production of excessive quantities of permanent gases from the light oil vapor formed which would normally result from the increased temperature and pressure is claimed to be prevented by the cooling of the vapor in the cool zone.

This temperature reduction may be produced by cooling the upper part of the still by exposure to the atmosphere or to artificial air currents or by cooling the vapors in other ways, but the best method is to cause the cooling medium to act on the zone which is naturally cooler than the other parts of the vapor space as that is the

point at which the vapors contain a maximum amount of light oil vapors As the mere heating of the heavy oil under pressure produces little light oil, and appears to aid the production of carbon, the volume of oil in the still should be small relatively to the vaporizing area, and the oil should be kept in constant circulation to bring each part to the vaporizing surface as rapidly and as frequently as possible. Further, if the heavy oil is passed slowly over the heated portions of the still, it is liable to be cracked too "fine," with the resulting release of a large proportion of permanent gases, and the simultaneous deposit of carbon. The heavy oil is positively circulated at such a speed that it cannot be suddenly heated or overheated at any point, and thereby the formation of carbon is greatly restricted. It is particularly advantageous to circulate the oil when the temperature of the oil is raised above that normally employed

Suspended from the top of the still *A* (Fig. 82) is a gas and vapor collector which is a large, tubular container *b*, perforated at its bottom and sides, the interior being in communication with the pipe *c*, which is telescopically connected to the cylinder *d* mounted on top of the still. This cylinder is connected to an adjustable pressure relief valve.

From the pressure relief valve the gases and vapor flow to an expansion chamber and then through a pressure

Fig. 82. — Transverse cross section of Jenkins' still, showing vapor collector.

relief valve to a condenser from which gasoline and other light products may be drawn. The gas and vapor collector is of double walled construction and has an inner wall *e* and an outer wall *f* between which extend a series of open-ended tubes *g* (Fig. 83), which allow vapor from the still to enter the collector. The pipe *c* is similarly double walled so that water or other cooling medium may be forced between the walls *h* and *k* of the collector. In order that circulation may be effected, partitions *m* (Fig 83) are arranged between the walls along the upper side of the collector and these partitions are extended between the walls of the pipe *c* (Fig. 82) on each side of it. The collector *b* (Fig. 82) is arranged quite near to the

Fig. 83.

level of the liquid in the still *A* and in the coolest part of the vapor zone. As the proper location of the collector depends in part on the nature of the oil used, as well as on the temperatures and pressure employed, the collector is arranged so that it can be raised and lowered in the still. For this purpose the pipe *c* (Fig. 82)

is mounted on a piston P adapted to slide to and fro in the cylinder c. In order to allow of this sliding movement of the pipe c, sliding connections are provided between the pipe c and the inlet and outlet pipes R and S for the cooling medium. These sliding connections consist of two pipes T and V having communication with the spaces between the walls of the pipe c on either side of the partition m (Fig. 83) and carrying stuffing boxes W and X for receiving the ends of the pipes R and S. The piston with the collector and other parts is raised and lowered by means of the tube Y which passes through a stuffing box Z at the top of the cylinder c so that it may be clamped in any desired position by means of set-screws. This tube is closed at its upper end but is provided between its ends with an aperture Y' through which the vapor from the still can pass into the pipe leading to the pressure relief valve.
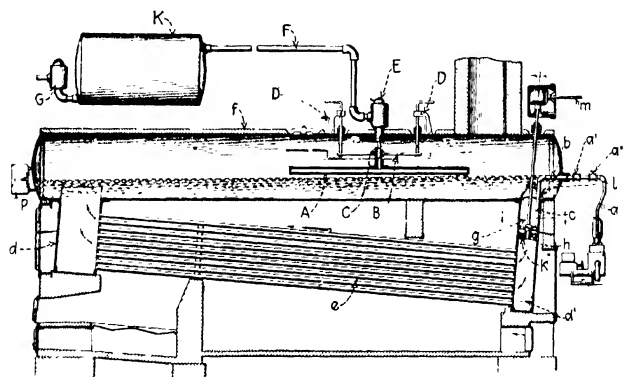
Fig. 84. — Jenkins' tube still with positive circulation of oil.

Details of the arrangement of the Jenkins still [1] and circulating tubes, equipped with a vapor collector of the type described above, are shown in Fig. 84. The process may be continuous.

The heavier hydrocarbon oil is pumped from the source of its supply through the feed pipe a, Fig 84, in which is check valve a', control valve a'', and through the inlet pipe b terminating in a downwardly directed portion c inside the still. The still is a strongly reinforced tank, having depending legs d and d', connected by a series of tubes e, which slope upward. The rear or lower leg of the still is an enlarged chamber d', which is connected to the barrel f by a circular passageway in which is mounted a propeller upon a shaft having a bearing at its lower end upon the spider construction k. The shaft passes through the spider l and out of the barrel through a stuffing box. It is equipped at its top with a bevel gear in mesh with which is another bevel gear upon a power shaft m. Below the still is a fire box. The supply of heavier hydrocarbons flowing in through feed pipe a controlled by valve a'' and being directed behind the propeller h is mechanically forced or

[1] J. S. C .I. 1917, 704; Chem. Abs. 1918, 1926; U. S. Patent 1,226,526, May 15, 1917; British Patent 116,119, May 17, 1917, to U. S. Jenkins. See also U. S. Jenkins, French Patent 485,774, Feb. 6, 1918.

pumped downwardly in leg *d'* and then upwardly through the tubes *e* and through the leg *d* and into the barrel *f*. This positive driving or pumping of the fluid causes a controlled and rapid circulation of the entire liquid contents of the still around or back through the barrel *f*, down leg *d'*, up through the tubes, through leg *d* and back into the barrel again.

The leg *d* is made larger than the leg *d'*, the purpose of this being to accommodate the expansion of liquid, which takes place in the tubes *e*, particularly at or near their upper ends, and to prevent the possibility of a " flare back," which is apt to occur if the enlarged and foaming volume of hotter oil is confined in a leg of the same size as that which holds the cooler incoming oil. By the provision of enlarged leg *d*, as well as by the mechanically forced rapid circulation induced by the propeller *h*, this " flaring back " of gases and vapors into the lower leg *d'* is prevented. The liquid level is maintained constant. This is done by means of a level indicator and controller *p*.

The gas and vapor collector can be moved upwardly or downwardly, as noted, so as to take off vapors of different densities. To effect this adjustment, the pipe *C* is rigidly connected at one end to the gas and vapor collector *A* and its opposite end passes through the journal in the arm *B* and is provided at its extreme end with an outwardly extending flange to rest on the arm *B* so as to move upwardly with it. For raising and lowering the arm *B* and gas collector *A*, two rods are provided which pass through stuffing boxes and then through openings in the supporting arms *D*. These are provided with set screws.

The liquid contents of the still, as noted, are rapidly circulated through the barrel, depending legs and tubes of the apparatus, while a brisk fire is maintained on the grate. The result will be the release of gaseous and vaporous products and the generation of pressure in the apparatus, evolved gases and vapors collecting in the space above the constant liquid level in the barrel *f*, where they suppesedly arrange themselves, at least temporarily, according to their densities — that is to say, the lighter gases and vapors will take position near the top of the barrel and the heavier gases and vapors collect below them, so that the average density of the gases and vapors at different levels will be different. The pressure is controlled by valve *E*. By controlling pressure, temperature and rate of circulation in the apparatus, according to Jenkins, the conditions required for the complete transformation of the heavier hydrocarbons can be obtained.

For example, if the pressure relief valve is set at 200 pounds, a constant pressure of approximately 200 pounds will be maintained in the apparatus, and the transformations which will occur take place continuously, new heavier hydrocarbons being supplied as required through feed pipe *a* to maintain a constant liquid level in the barrel. In actual operation, the entire process is said to progress smoothly and quietly, the oil flowing rapidly through the apparatus, and condensable gases and vapors continuously flowing off through the collector *A*. The gases and vapors passing through the pipe *F* are permitted to expand against a low pressure of about ten pounds, controlled by the pressure relief valve *G*, in the expansion chamber *K* and are thus effectively reduced in temperature, after which they are passed through condensers.

By means of the mechanical circulation, the deposit of carbon in these tubes is said to be rendered practically impossible. This deposit, which is unavoidable and constitutes a very serious and expensive trouble in the operation of ordinary petroleum stills, is caused, it is said, by the fact that the oil cannot be made to pass rapidly enough over the heated surfaces and hence is cracked too extensively, with the release of a large proportion of permanent gas and the resulting deposit

of carbon. By means of the positive circulatory system, the oil may be made to circulate at any desired speed, preventing the charge from being suddenly heated or overheated at any point.[1]

The Isom Process

In the **Isom** process[2] the purpose also is to subject oil to temperatures and pressures under such conditions that there will be no deposition of carbon upon the highly heated surfaces. A horizontal cylindrical reservoir, C (Fig. 85), similar to a still, is in series with
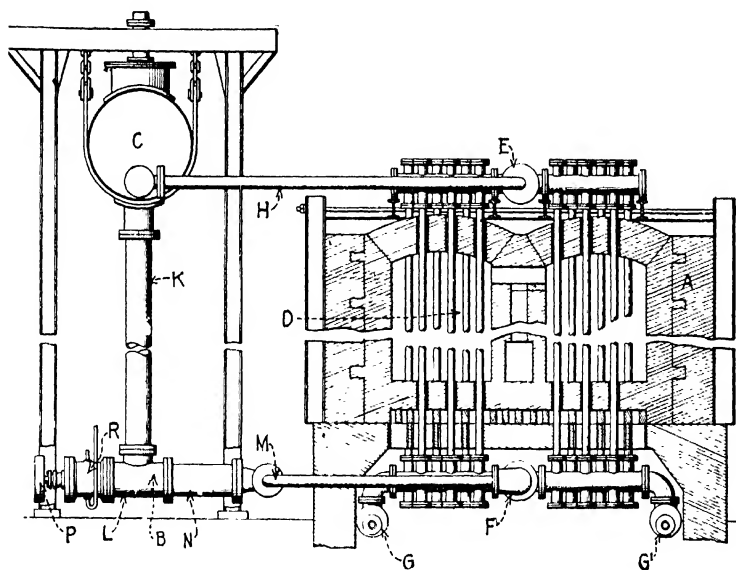
Fig. 85.—The Isom tube still.

multiple-connected heating tubes D. The oil is passed through this battery of tubes in a furnace A, being constantly circulated from the reservoir C through the tubes D, by means of a forcing device B. The tank C is connected to a condenser. High pressure is maintained throughout reservoir C, tubes D and condenser. It is stated that the rush of liquids through the heating tubes constantly sweeps them clean and free from carbon deposit. The heating tubes, or fire tubes, are in a furnace setting which is located apart from the drum or reservoir.

[1] See also U. S. Jenkins, U. S. Patent 1,321,749, Nov. 11, 1919
[2] U. S. Patent 1,285,200, Nov. 19, 1918.

A continuous supply of fresh oil to the reservoir renders the process continuous The upper manifold E is placed above the roof of the flues. The lower manifold F is similar to the upper one, and the heating pipes extend vertically between the respective branches on the laterals of the upper and lower manifold and through the roof and floor of the flues. The upper and lower branches of the manifolds are closed by removable plugs. Traps G, G' are provided at the respective opposite ends of the laterals of the lower manifold and are each connected to the end of each of the adjacent laterals by elbows in such manner that the solid and semi-solid contents of the oils tend to settle into the traps. Each trap at its opposite ends has draw-off pipes provided with turning plugs for draining the trap. From each end of the main of the upper manifold, a return pipe H leads to the corresponding end of the supply tank C, by means of which oil is continuously returned from the heating pipes to the tank. From the center of the tank a main k leads downwardly to the casing L of the oil forcing apparatus from which the oil is distributed by
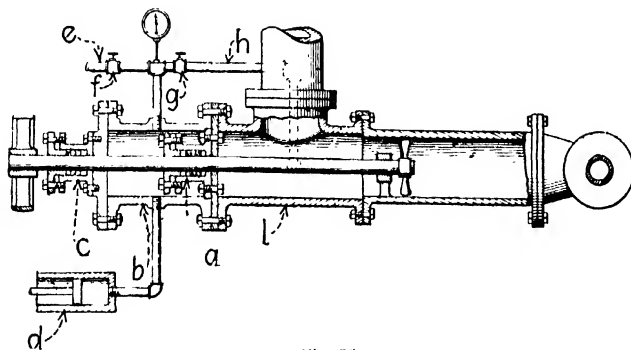
Fig. 86.

branch pipes M, to the opposite ends of the main of the lower manifold. The oil forcing apparatus consists of a spiral conveyor or screw-propeller, the shaft of the conveyor being provided at its outer end with a driving pulley P. By rotating the screw-propeller the heavy oil is circulated rapidly from the forcing apparatus upwardly through the heating pipes to the tank, and back through the downcomer to the forcing apparatus. Because of the high pressure a special precaution must be taken for preventing the leakage of oil about the shaft since the oil being above the ignition temperature would immediately inflame on exposure to the atmosphere. To avoid difficulty of this kind a stuffing box a, Fig 86, is provided about the shaft, and is in turn enclosed in a housing b, which has a stuffing box about the shaft at c. Relatively cold oil is circulated through the housing at a pressure somewhat in excess of the pressure within the casing so that if there is any leakage past the stuffing box, it will be of the cold oil rather than the hot oil. For this purpose a pump d is connected to a tank containing oil of the character being treated and to the housing b. From the housing the oil is led to the interior of the casing l, where it mingles with the oil being treated. To maintain the level of the liquid in tank C, the oil is supplied in this manner but normally is not alto-gether sufficient for the cooling of the housing. Therefore a waste pipe e is pro-vided which leads to the supply of oil. Valves f and g control the return or

waste-pipe e and the pipe h respectively and may be used to regulate the amount of oil introduced into the cracking system. The supply of oil to which the pump d and return pipe e are connected is of sufficient size to avoid materially heating it by the return of oil. Sufficient circulation of the oil through the housing is maintained to prevent heating to a dangerous temperature so that it is immaterial if there be leakage past the packing C.

The upper manifold supports the weight of the lower manifold and the heating pipes and is itself supported upon I-beams, forming part of the reinforcing structure of the furnace. Thus the pipes D are free to expand with the temperature.

The only surfaces subjected to heat are all vertical and constantly swept by the current of oil so that there is little or no tendency for carbon to accumulate and their heat-conductive capacity is therefore not diminished nor are the pipes in danger of overheating. There are no joints within the heated zone but only straight pipes and on account of the clean-out plugs or plates referred to the pipes may be readily cleaned. The greater proportion of the solid matter is deposited in the traps from which it may be removed and any matter accumulating in the lower header may be removed through handholes.

CHAPTER IX

CRACKING IN STILLS UNDER PRESSURE

Dewar and Redwood Process

Dewar and **Redwood** [1] crack heavy oils and residues by heating under pressure and condensing under pressure. The use of an extraneous gas to create additional pressure in the still is also mentioned.

These investigators, who apparently were the first to simultaneously distill and condense under pressure, call attention to the very large résidue frequently obtained in distilling mineral oils, such as natural petroleum or similar oil made from shale, coal or other bituminous substance, in order to separate the lighter oil suitable for lamps or other purposes from the heavier oils. They refer to the attempts to obtain lighter oils from these residues or from heavy natural petroleums by causing the compressed vapor generated in the still to pass a heavily loaded valve or a regulating stopcock to the condenser, so that the vaporization might take place under considerable pressure. They state that it had also been proposed to arrange the still with its upper part cooled so that the less volatile portions of the vapor may become more or less condensed and fall back into the hot liquid below, this mode of operating then being commonly termed " cracking." Both these methods are considered objectionable, the former on account of the irregularity of the distillation, and the latter on account of the waste of heat in conducting the cracking process, and the slowness and insufficiency of the results.

The method used by Dewar and Redwood, however, consists in conducting the distillation in such a manner that regular vaporization and condensation under high pressure results, and at the same time cracking duly takes place. For this purpose a still and a condenser are arranged in free communication with one another without interposing any valve, but a regulated outlet for condensed liquid from the condenser is used. The space in the still and condenser that is not occupied by liquid is charged with gas under considerable pressure. Carbonic acid gas, or other gas that cannot act chemically on the matter treated, may be employed.

[1] British Patents 10,277, June 24, 1889; 13,016 (1890); 5971 (1891); U. S. Patents 419,931 and 426,173 (1890).

The distillation and condensation being thus conducted under considerable pressure, which can be regulated at will, there is obtained from the heavy residue a quantity of light oil suitable for illuminating and other purposes, which products cannot be so successfully obtained by distillation under atmospheric pressure. The still head or upper part of the still is designed so as to operate according to the cracking method above referred to, the cracking in this case taking place under high pressure, instead of being carried on under atmospheric pressure.

Above the combustion chamber B (Fig. 87) is placed a metal retort C which is enclosed within a refractory casing C^1 to protect the metal from excessive local heating. The encased retort is situated in a heating chamber B^1 into which the hot products of combustion ascend by side ports B^2 and from which they pass by central ports B^3 into a flue B^4 communicating with a chimney. The front part of the retort C communicates freely with a still head C^2 provided with a pressure gage C^3 and safety valve C^4. The exposed end of the retort C is closed by a removable cover C^5 provided with a glass gage to show the level of the liquid in the retort. D is a pipe coil situated in a tank D^1 in which circulation of water is maintained. The upper end of the coil D communicates by a pipe with the still head C^2 and its lower end opens into a hollow column D^2 which is provided with a glass gage D^3 and has at the bottom an outlet pipe D^4 furnished with a stop cock or valve. A pump forces oil to be treated by a pipe E^1 into the retort C, this pipe normally extending nearly to the farther end of the retort. By another pipe E^2 furnished with a valve, the contents of the retort can be drawn off, or this pipe may communicate with a second retort which in like manner may be connected with a third so as to form a series of any required number. Air or other gas is forced by a pipe F^1 into the still head C^2 or into any other part of the apparatus which is in communication with the still head. The retort C being partly charged with oil, and the spaces in the retort C in the still head C^2 and in the condensing coil D and the column D^2 being charged with air or gas to the desired pressure, the retort is heated, vaporizing the oil under pressure. The oil vapor is condensed in passing through the coil D and the liquid distillate collects in the column D^2 and is drawn off either continuously or intermittently into suitable receptacles in which such gas as may be dissolved in the liquid is liberated and can be collected. By a pipe and a cock or a suitably loaded safety valve D^5 gas may be withdrawn from the space above the liquid in the column D^2.

There may be several sets of stills and condensers in communication with the oil and gas pumps, or with each other, requisite valves being

provided in the communicating pipes so that the several stills may be worked simultaneously or in rotation.   From time to time the cover C^5 of the still may be removed to clear out residue.   During the dis-
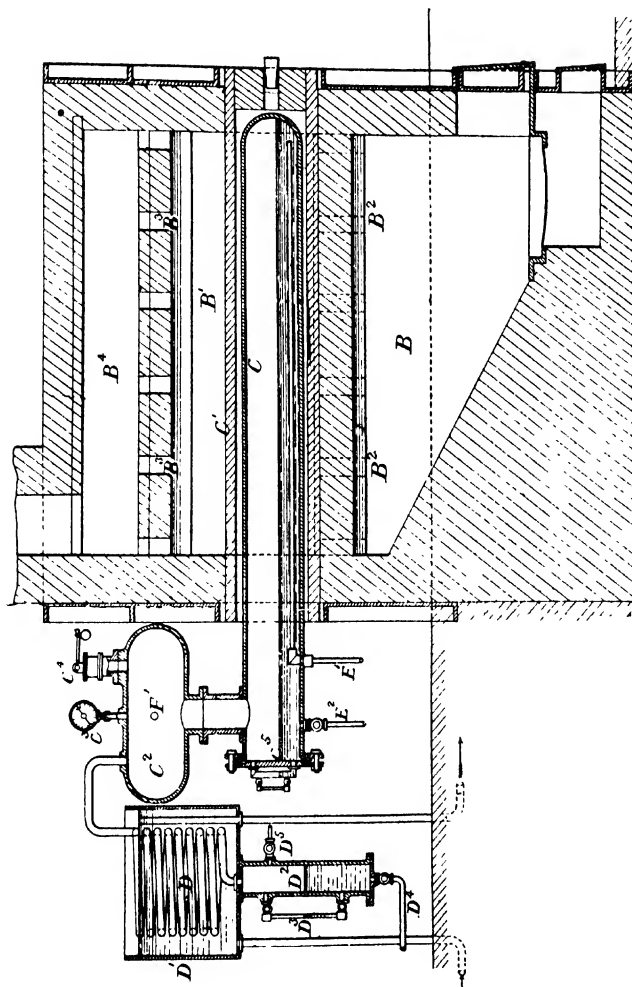
Fig. 87. — Dewar and Redwood pressure still.

tillation any vapor condensed in the still head C^2 or such liquid as may prime up into the still head flows back into the body of liquid in the retort.   By regulating the heat and pressure to which the retort is subjected, the character of the distillate may be varied and thus oils

more or less light can be obtained to suit various uses. Also the proportions of the parts may be varied and if necessary cooling may be applied to the still head C^2.

The method and apparatus are applicable not only to petroleum and other oils, but also to substances generally, from which oils can be distilled, for instance, colophony and other resins. The substances treated by this process, Dewar and Redwood state, should customarily be as free as possible from water so as to avoid generation of steam at high pressure. In some cases the operation is accompanied by production of permanent gas which, being incapable of condensation, would accumulate and produce abnormal pressure. A relief valve should therefore be provided to allow escape of this gas from time to time.

CHAPTER X

CRACKING IN STILLS UNDER PRESSURE — *Continued*[1]

The Burton Process

Burton[2] distills fuel oil and gas oil under a pressure of 4 to 5 atmospheres and also condenses the distillate under pressure in equilibrium with the vapor pressure obtaining in the still. A saturated gasoline is said to be obtained.

* Burton notes that the demand for gasoline has induced a large increase in the supply by improvements in the method of distilling from crude petroleum the naphthas, the boiling points of which range from about 75° F. to 350° F. (27°-177° C.). This leaves the illuminating oils, the boiling points of which range from about 350° F. to about 600° F. (177°-316° C.) and the lubricating oils and waxes and, as residue, fuel oil and gas oil, with boiling points ranging from about 600° F. to 700° F. (316°-371° C.). The increasing demand for gasoline has induced attempts to obtain it from this residue; but these attempts, while successful in producing gasoline, have invariably, it is stated, as the result of lowering the boiling point, changed the general formula of the paraffin group ($C_nH_{2n} + 2$) to that of the ethylene group (C_nH_{2n}), rendering the product unmarketable on account of its offensive odor, for the removal of which no suitable treatment has been found. A method of treating the fuel and gas oils, for obtaining a low boiling point product involves subjecting the liquid to be treated to a temperature sufficiently high to secure so-called destructive distillation, and conducting the resultant vapors through a condenser by way of a pipe or conduit connecting it with the still, but having a loaded valve interposed in the conduit between the condenser and still to maintain pressure in the latter of the vapors of distillation on the liquid. While this practice produces the desired effect of yielding liquids of lower boiling point, the condensed product is found to have been converted into distillates belonging to the objectionable ethylene group referred to. The object is to avoid conversion of the petroleum of the paraffin series into products belonging to the ethylene series. This is said to be accomplished by raising the boiling point of the liquid residue and increasing the heat influence on it while undergoing distillation by maintaining back pressure on the liquid of the vapors from distillation, and also maintaining the vapors themselves under pressure throughout their course from the still through the condenser and while undergoing condensation

In Fig. 88 still *A* for the liquid residue to be treated surmounts a fire chamber and is equipped with a safety valve *B* to relieve excessive pressure, a pressure gage,

[1] See also Chapter III, page 72, on Refinery Practice.

[2] Chem. Abs. 1913, 888, 1607; 1914, 2944, 3235; Chem. Abs 1916, 1594; British Patent 29,862 (1912); Norwegian Patent 26,668, Feb. 14, 1916; U. S. Patent 1,049,667, Jan. 7, 1913.

and a temperature gage *C*. A conduit *D* leads from the top of the still and inclines upwardly (to induce the return flow into it of unvaporized portions of the liquid) to a condenser *E* the tank of which is provided with a lower draw-off cock. The condenser coil discharges at its lower end through a pipe extension into a receiver for the products of condensation. In this pipe, and thus beyond the discharge-end of the coil, is contained a shut-off valve *F*, and it is desirable to equip the coil with a relief valve *K* on the upper end of a pipe rising from near the lower end of the coil through the top of the condenser tank, for relieving the gas pressure which is liable to accumulate in the coil and obstruct the action of the apparatus. The valve *F* is normally closed. From a supply of the liquid residue contained in the
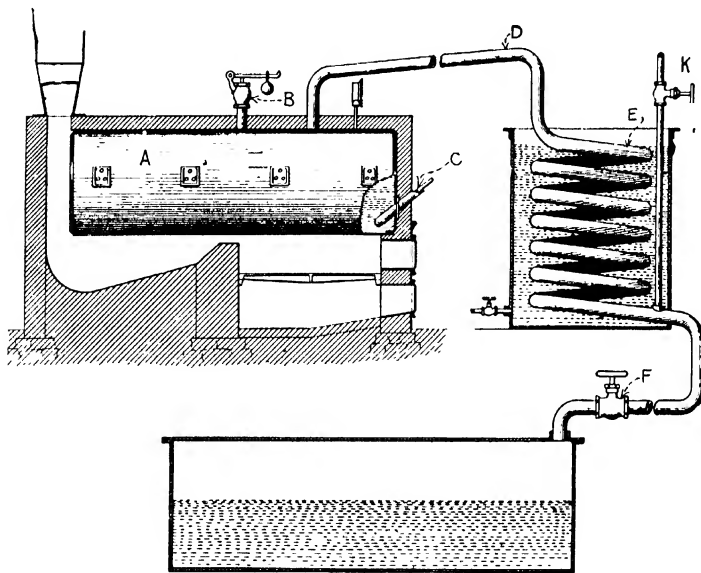
Fig. 88. — Burton pressure still.

holder *A* heat from the fire chamber distills the volatile constituents, and the resultant vapors course through the conduit *D* and coil *E* in which they are condensed. With the valve *F* tightly closed against the escape of the products of condensation, the vapors of distillation accumulate and exert a high pressure amounting from about 4 to about 5 atmospheres upon the liquid in the still, raising the boiling point from 500° F.–600° F. (260°–316° C.) to 750° F.–800° F. (401°–427° C.) and this pressure of the vapors combined with their heat increases the conversion of the high boiling members of the paraffin series into the low boiling members of the same series. The valve *F* is opened from time to time to draw off the products of condensation into the receiver. In fact, the intervals of drawing off should be sufficiently frequent to avoid filling the coil with liquid. The resultant gasoline is said to be a product belonging to the paraffin series, the same as the petroleum residue from which it was distilled.

An improvement in this process consists [1] in distilling to dryness, at atmospheric pressure, the residue from the pressure distillation, uniting this atmospheric distillate with the residue from a previous pressure distillation and subjecting the whole to the heat-pressure treatment. In this way high yields of gasoline are said to be obtained.

The pressure distillation is continued until the residue in the still is reduced to a thin syrup-like consistency, and the original charge has been reduced to from 30 to 40 per cent of its bulk. In the meantime, it is desirable to open, from time to time, a relief valve in the upper
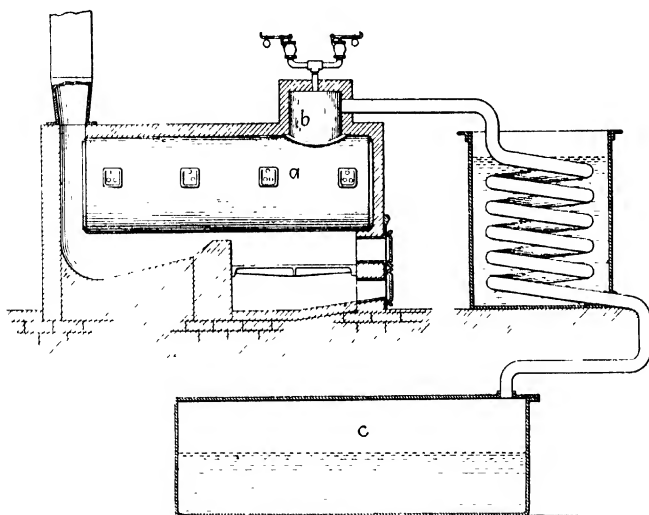
Fig. 89.

end of a pipe rising from near the lower end of the condenser coil, for relieving the gas pressure. The residue is withdrawn from the still *A* (Fig. 88) and is introduced into a second still *a* (Fig. 89) heated by a furnace and provided with a vapor dome *b* equipped with a pressure safety valve and a vacuum safety valve. A pipe connects the vapor dome with a condenser coil discharging from its lower end into a receiver *c*. The contents of the still are maintained under atmospheric or approximately atmospheric pressure to distill the volatile constituents of the contents, which are conducted off and condensed, and the products of condensation accumulate as a yellowish liquid in the receiver. This procedure is carried on until the original contents of the

[1] Burton Chem. Abs. 1915, 2452; Chem. Abs. 1916, 263A; Chem. Abs. 1917, 207; British Patent 6593, Mar. 16, 1914 (Standard Oil Co); Holland Patent 1656, Oct. 16, 1916 (Standard Oil Co.); U. S. Patent 1,105,961, Aug. 4, 1914.

still *a* have been reduced to a condition of dryness, the distillate accumulated in the receiver amounting to about 95 per cent of the charge in the still *a*.

The liquid of condensation in the receiver is withdrawn and introduced into the still *A*, Fig. 88, or into another like it for separate treatment, and is there subjected to the original process. The resultant distillate is claimed to be a low boiling point product, belonging to the paraffin series. Instead of treating the contents of the receiver *c* (Fig. 89) separately in a still *A* (Fig. 88) it is suggested that they be mixed with the original residue. By following the last named practice, about $63\frac{1}{2}$ per cent of the original charge in still *A* is converted into gasoline, about $1\frac{1}{2}$ per cent going off in the form of gas, which is used as fuel. This leaves somewhat less than 35 per cent of the original charge as residue to be treated in still *a* from which about 95 per cent is distilled, leaving about 5 per cent as dry residue or coke; and this distillate, being turned back into still *A* for treatment with the charge introduced therein for the original treatment, again produces in the first still the same yields of about $63\frac{1}{2}$ per cent of gasoline and about 35 per cent of residue. In this way the practice may be carried on endlessly by the addition of fresh charges into the high-pressure still. Thus practically all (not considering the incidental losses) of the original high boiling point product first treated by the process practiced in still *A* is said to be converted into gasoline of the same paraffin series or group as that of the original residue. The low boiling point product referred to as gasoline, is crude gasoline, which has to be prepared for the market by first treating it with sulphuric acid and then re-distilling to produce the finished deodorized gasoline. The sulphuric acid treatment entails a loss of about $1\frac{1}{4}$ per cent.

It is stated [1] that the atmospheric destructive distillate produced as described above consists of hydrocarbons whose viscosities are very low in consideration of their respective gravities.

The distillate is said to consist of a mixture of oils of varying gravity and chemical composition, in large part members of the upper range of the paraffin series, but including also some proportion of unsaturated hydrocarbons, asphalts, cyclic compounds and other products and by-products of petroleum distillation, the exact constitution being dependent upon the nature of the raw material used in its manufacture. A typical series of fractions taken from the still at intervals during a run of the latter will show the following relations between the gravity and viscosity of the fractions:

Baumé gravity	Viscosity at 100° F. (Saybolt viscosimeter)	Baumé gravity	Viscosity at 100° F. (Saybolt viscosimeter)
28.9	36	15.8	76
26.5	38	15.2	88
23.8	42	15.0	89
21.5	45	11.7	97
21.1	51	11.1	105
20.2	52	13.2	110
18.7	58	13.0	116
17.8	62	12.0	158
17.2	65	10.8	198
16.7	66		

[1] Burton, U. S. Patent 1,167,884, Jan. 11, 1916.

Similar gravity-viscosity tables of some common petroleum oils made by other processes are as follows:

Oils made from California crude petroleum

Gravity	Viscosity at 100° F
18 8	449
20.4	235
20 6	339
21.6	446
21.8	167
22.5	439

Oils made from Kansas-Oklahoma crude petroleum

Gravity	Viscosity at 100° F.
25 0	235
26 0	490
26 0	165
26 5	445
27 5	400

By plotting graphically the gravity-viscosity curve of the fractions which make up the oil described and by plotting similar gravity-viscosity curves of the other oils given it is seen that over the whole range of its constituent fractions it has a considerably lower viscosity than other oils of the same gravity or density. In physical appearance and in chemical constitution it appears to be the same as other petroleum oils of the same gravity It may be filtered, treated with acids and alkalis, fractionated and subjected to the customary processes of petroleum refining in so far as is necessary to fit it for any particular use.

A. S. Hopkins [1] practicing the Burton process, uses a special reflux condenser, which utilizes the latent heat of condensation and also the specific heat of the vapors, to preheat fresh oil for the still. This is said to greatly assist, also, in controlling the gravity of the light oils produced. It is set forth that in order to obtain a maximum yield of the desired distillate in carrying out the Burton process, it is important to make a separation of the vapors leaving the still, immediately condensing and returning to the still for further treatment any fractions of higher boiling point. The separation is sometimes effected by an air condenser in the form of a relatively large upwardly inclining vapor conduit known as a dephlegmator or run-back, which is surmounted by a condenser proper. This consists of a number of exposed pipes so arranged as to drain into the run-back. From the upper end of this last condenser the vapors which have escaped condensation pass to the water cooled coils which drain into a receiver for the distillate. The use of this apparatus entails a considerable heat loss, the heat units

[1] U. S. Patents 1,199,463 and 1,199,464, Sept. 26, 1916; Chem. Abs. 1916, 2984.

given up in so condensing the heavier vapor fractions being dissipated
to the atmosphere, and changes of atmospheric conditions modify the
operation of these fractionating condensers.

Hopkins' modification is essentially as follows:

The heat units given up in condensing the heavier fractions are utilized to
preheat a fresh supply of stock which is to be fed to the still for treatment. The
fractionation of the distilled vapors is controlled independently of weather condi-
tions.

In Fig. 90, surmounting the fire box and combustion chamber is the still A
from the upper side of which and inclining upwardly leads the dephlegmator, run-
back, or vapor outlet pipe B at the upper end of which is located the reflux condenser
C. From the upper end of this condenser there leads a vapor outlet pipe D by
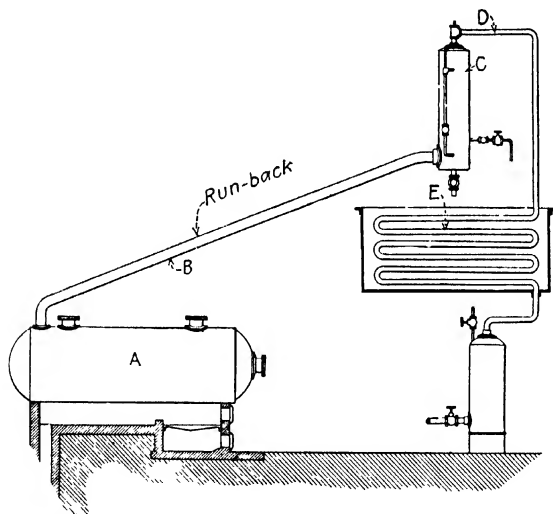
Fig. 90. — Modification of Burton process, by A. S. Hopkins.

which the vapors are carried through a condensing coil E. A drain pipe carries the
condensed distillate from the coil into a drum from which the contents may be drawn
from time to time. For controlling the escape of the incondensable gases by which
the desired pressure is maintained upon the still, there is a valved escape pipe tapped
into the upper portion of the receiver. The construction of the fractionating con-
denser C is shown by Fig. 91, from which it will be seen that this is a vertically
arranged casing or shell F in which there are arranged transverse tube sheets G
having tubes H expanded in it. By this construction the interior of the shell F is
divided into three compartments, a lower compartment, which is in communica-
tion directly with the run-back pipe, an intermediate compartment, which lies be-
tween the tube sheets and an upper compartment, which communicates with the
lower compartment through tubes and has tapped into it the outlet pipe D. Near
the lower end of the intermediate compartment an oil supply pipe is tapped into it,

this pipe communicating with the pump or source of oil under pressure. A hand controlled valve and an automatic check valve are arranged in the supply pipe adjacent to the condenser. Next to the upper end of the intermediate compartment a transfer pipe K is tapped into it, this pipe leading downwardly and reentering the shell of the condenser at its lower end to communicate with the lower compart-

ment. It is desirable that a cut-off valve be located in the length of the transfer pipe. The bottom of the lower compartment is slightly below the point of entrance of the run-back, and for the purpose of draining out this sump there is a valved drain pipe M. A thermometer having its operative portion lying within the upper compartment is extended outwardly through a T-joint in the vapor outlet. A second thermometer may be placed in the transfer pipe

The operation is as follows The mixed vapors rising from the still pass outwardly through the dephlegmator B, which, according to ordinary practice will be uninsulated and will, therefore, serve to some extent as a fractionating condenser removing the very heavy vapors and returning them to the still This operation is not necessary, however, since it is possible to thoroughly insulate the run-back, depending wholly upon the condenser C for the desired effect After passing through the lower vapor compartment of C, the gases traverse the cooling tubes H, transferring their heat through the walls of the latter to the oil within the intermediate compartment, the higher boiling point fractions being condensed and caused to drain downwardly into the lower compartment and from the latter through the run-back to the still to be again subjected to cracking The desired fractions, however, pass through the fractionating condenser in the form of a vapor

Fig. 91. — Heat exchanger for Hopkins process.

and by the conduit D are carried to the main or water cooled condenser. By the indications of the temperature as shown by the thermometer, the maximum boiling point of the vapors passing may be readily observed, and by manipulating the control valve V, thereby increasing or decreasing the flow of cooling oil into the intermediate compartment, the quality of the distillate forming vapor may be changed at will.

During the process of distillation, the oil within the intermediate compartment gradually moves upward, and entering the upper end of the transfer pipe is conveyed by the latter directly into the vapor (lower) compartment, its temperature at the time of its entry into this compartment ranging from 400° to 500° F. In this latter com-

partment the lower boiling point fractions of the inflowing oil are converted into vapor, their sudden expansion having a secondary cooling effect on the mixed vapors from the still, thereby lessening the amount of heat to be transmitted through the vapor tubes H and increasing the efficiency of the condenser. A considerable percentage of this oil is converted into the desired fractions within the lower compartment itself, while the remainder mixed with the condensate from the tubes H drains back through the run-back to the still for further treatment.

The loss of heat is reduced to a minimum, it being possible to thoroughly insulate or jacket both the run-back and the condenser C and thereby free the apparatus entirely from the effect of atmospheric changes   By observing the indications of the thermometer and properly regulating the valve V, it is possible to accurately control the boiling point of the distillate reaching the receiver, and to counteract the effect of uneven firing under the still   The fresh stock fed into the oil supply pipe is so thoroughly preheated during its passage through the intermediate compartment that upon entering the vapor compartment all of the desired lighter fractions which it may contain are vaporized and there is reason to believe, that a certain limited amount of cracking takes place within this chamber also. Since all of the oil fed in by the oil supply pipe is in effect added to the charge of the still, it will be seen that the capacity of the latter is increased to this extent, and since the quantity of fuel required and the time for completing a run of the still does not increase proportionately, it may be said that the apparatus is not only of greater capacity but has a higher efficiency.

E. M. Clark [1] connects the vapor lines and also the distillate discharge lines of several Burton stills " in multiple," that is, by means of headers common to all the stills. The result is that when a fresh still has been brought to a vapor temperature of about 250° F. (121° C.), the pressure obtaining in the other stills connected to the same header as the fresh still may be immediately applied to the fresh still. This prevents distillation, in the latter, of vapors at a relatively low pressure (as would otherwise be the case) and tends toward keeping at a minimum the amount of low grade distillate produced. [2]

It is stated that in distilling residue of petroleum distillation, such as gas oil or fuel oil, at atmospheric pressure, vaporization begins at a temperature of about 250° F. (121° C.) and all will distill over at a temperature upward of 650° F. (343° C.). In distilling this residue under a pressure upward of three atmospheres producing a range of temperature of about 650° F. to 850° F. (343°–455° C) a quantity of fixed gas amounting to about 2 per cent of the stock charged into the still is produced. A battery of stills (usually ten or more) is used. Each still is provided

¹ J. S. C. I. 1916, 34; 1915, 346,415; U. S. Patent 1,132,163, March 16, 1915; Chem. Abs. 1916, 1929; U. S. Patent 1,129,034, 1915; British Patent 1226, Jan. 26, 1915.

² See also Chem. Abs 1916, 1789; Swiss Patent 72,729, July 1, 1916 (Standard Oil Co.); Danish Patent 21,088, Mar. 3, 1916. Addition to Danish Patent 19,216.

with its own condenser and with separate equipment involving a drum for receiving the products of the condenser and separating the water and gas from the condensed distillate, and a meter for measuring this distillate in its course to storage. Both the gas and distillate discharge lines are equipped with valves for controlling the rate of discharge. When a still in the battery is freshly charged and fired, the valves in these discharge lines are closed. As the firing of the still is continued and the temperature of its contents rises to about 250° F. (121° C.) water and petroleum vapors distill over through the condenser into the receiving drum. As
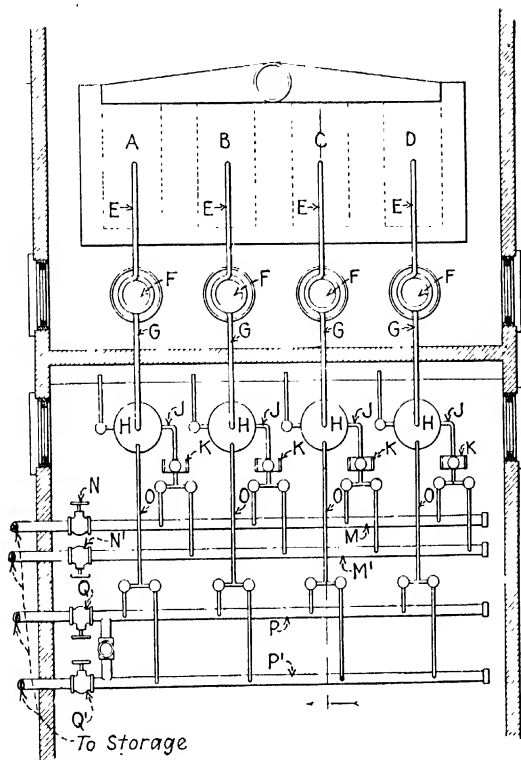
Fig. 92. — Battery of pressure stills connected in multiple according to E. M. Clark.

the distillation proceeds small quantities of uncondensed vapor or gas collect in the apparatus, and after a quantity of low grade distillate (upward of about 8 per cent of the stock charged) has been produced, sufficient gas has collected in the apparatus to create a pressure of vapors through the condenser. Continued firing of the still raises further the temperature of the contents, producing increasing formation of gas and building up of pressure in the apparatus. When the desired temperature (about 650° F.) (343° C.) and pressure (say about 70 to 75 lbs.) have been attained, the gas in the apparatus is allowed to escape slowly through a valve

in its discharge line from the top of the receiving drum.   Vapors will then begin
to come over through the condenser, and high grade liquefied distillates will be
produced and be discharged from the receiving drum through the meter into
storage. Since this distillation process is necessarily slow, the formation of gas
is very gradual. Production of the high grade distillate is dependent on constant
pressure on the apparatus. A slight drop in pressure causes the vapors to come
over more freely and produces low grade distillate, and, conversely, even a slight
increase in pressure entirely stops the flow of vapors with resultant danger to
the apparatus. It is desirable to have a process for controlling the discharge of
gas and liquefied distillate so that a minimum amount of the latter of low grade
and a maximum amount of high grade shall be produced.

A method of safeguarding the apparatus used is also very necessary by prevent-
ing any extraordinary excess of pressure, and also to so apply a gas pressure of about
70 to 75 lbs., from stills in the battery that are running, to the contents of a still when
freshly charged as to prevent distillation of the contents of the fresh still before
the desired temperature has been attained

In Fig. 92 four stills, denoted respectively A, B, C and D, are indicated
These stills communicate with a stack common to all, for carrying off products of
combustion from the furnaces under the stills. A vapor pipe E leads from the
top of each still to the upper end of the water cooled coil of a separate condenser
F, and from the bottom of each coil leads, through the inner wall of a housing, of
which the side walls are shown, a pipe G for conducting the products of the con-
denser, composed of liquefied distillates and the light, gaseous products of distil-
lation which have not yielded to the action of the condenser, into a separate drum
H at the top of the latter.   From the bottom of each drum leads a pipe J contain-
ing a meter K for measuring the liquefied distillate and having two valved branches
These lines discharge, respectively, into header-pipes M and M' closed at one end
and containing similar shut-off valves N and N' respectively.   The header-pipes
discharge to storage tanks. Each drum discharges gas from its upper end through
a pipe O having two valved branches and leading, respectively, into header-pipes
P and P', which are closed at one end and contain similar shut-off valves Q and Q'
respectively. These pipes also lead to storage-tanks (not shown).

Suppose that three of the stills, namely A, B, and C, are running at the
cracking temperature of upward of 650° F. (343° C) and under a pressure of
about 70 to 75 lbs. of the gases on the contents of the stills. The gases are dis-
charging into the header-pipe P' and are being held back by the partly closed
valve Q' in the latter to produce the required pressure of 70 to 75 lbs in that
header-pipe and throughout the apparatus of the running stills. High-grade
liquefied distillate is being discharged from the bottoms of the three respective con-
densers through the meters into the header-pipe N and through its partly open
valve N' to storage. The rate of this discharge is regulated by the valve N' in
the header-pipe N to maintain the required pressure throughout the apparatus and
discharge the distillate as it is produced. The three stills thus running are all sub-
ject to the same pressure. These stills, being connected by the header-pipes P'
and N, give a sufficient volume of gas and liquid distillate to make the rate of
their discharge easily controllable by the valves Q' and N'.

Suppose that the fourth still B has just been freshly charged and fired.
The still D is closed to the 70 to 75 lbs. pressure maintained in the
header-pipes N and P', and is open only to the header-pipe P which

conducts the gases to storage, or to the furnaces. The firing of this still is continued with resultant rise of temperature of its contents. At about 212° F. (100° C.) the watery portions of the charge are driven over. When the water has all been driven off, which is indicated by the temperature of the contents of the still B, the oil portion will begin to distill over at about 250° F. (121° C.). To stop this distillation and the resultant production of low grade distillate, the gas from the three other stills, that are running under a pressure of 70 to 75 lbs. in the header-pipe is allowed to exert its back pressure upon the contents of still D to stop the flow of vapors from the latter. In this way the pressure upon the contents of the freshly charged still is raised to that upon the stills A, B and C.

The firing of still D is continued until the temperature of its contents is raised to upward of 650° F. (343° C.) when that still will begin to drive over its gases through the condenser, into the header-pipe P', and the production of high grade liquefied distillate will begin. The high grade distillate produced is discharged into the header-pipe N in conjunction with that produced from the other running stills. The four stills are now running in conjunction, all subject to the same control and the same pressure influences. The sudden generation of excessive or dangerous pressure in one still is prevented by the connection of all through the header-pipes and open valves. Suppose also that a still, say A, has completed its run and is ready to be drawn off, cleaned and freshly charged. Its furnace fire is drawn, and it is shut off from the 70 to 75 lbs. pressure in the header-pipes P' and N and from the influence of the stills B, C and D. As soon as the gas that was held under 70 to 75 lbs. pressure in the equipment belonging to still A has been discharged, the tar or residual contents of the still are drawn off, and it is made ready to clean and receive a fresh charge. Each still in a battery is handled in this way after completing its run.

CHAPTER XI

CRACKING UNDER PRESSURE — *Continued*

Coast's Processes

The use of steam in cracking hydrocarbons to make gasoline has been the basis of a considerable amount of investigation in the past and a large number of petroleum technologists have recommended its use. A great many others have maintained that it possesses no advantages. Permanent gases and some vapors have also been applied to a considerable extent in methods for decomposing oils to make naphthas and burning oils, the idea probably being, in some cases at least, to effect a chemical " fixation " of these gases by the unsaturated hydrocarbons resulting from the heat decomposition of relatively heavy oils.

Coast employs, in this connection, both steam and gas, for example, natural gas. He therefore deals in one of his methods with the system " heavy oil vapor — water vapor — natural gas " and he manipulates this system in at least two different types of apparatus, first, pressure stills, and secondly, in tubes under pressure.

A rather unusual method is used to effect separation of light and heavy vapors in the dephlegmators, viz., direct cooling by means of steam, in some cases and, in others, fresh oil. In the case of the pressure stills a special water cooled device is used to prolong the life of the still bottom. In a type of pressure still used by Coast, a reflux air cooled condenser is in free communication with the still but the light distillate is condensed at ordinary pressures.

Devices for Protecting the Bottom of the Still

In Coast's process [1] a water cooled jacket is used to prevent the still bottom from becoming overheated.

In usual practice when high boiling point petroleum hydrocarbons are cracked in the ordinary cylindrical still, heavy coke forming fractions settle on the still bottom. The resultant coke or carbon is a good heat insulator; it prevents the free transmission of heat from the still bottom to the liquid, and it usually accumulates in a pile at some point directly above the fire. When a sufficient quantity of this coke has accumulated, a portion of the bottom of the still soon

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[1] U. S. Patents 1,252,999 and 1,253,000, Jan 8, 1918.

becomes red hot, and some immediate steps must then be taken to avoid a rupture at the overheated portion of the still. In actual practice, the still is usually permitted to cool and the coke or carbon is then removed. This procedure results in a loss of fuel due to the cooling and reheating of the still, the operating expenses are otherwise increased, and the average yield per hour is decreased.

Coast proposes to eliminate the danger by protecting the overheated portions of the still, thereby increasing the life of the still and permitting it to be operated continuously for a considerable period of time without removing the coke or carbon. •

In Fig. 93, A' is a diagrammatical view of a cracking apparatus, showing a shield. B' is a horizontal section, showing the heating chamber and the shield mounted. C' is an enlarged horizontal section. showing the interior of the shield.
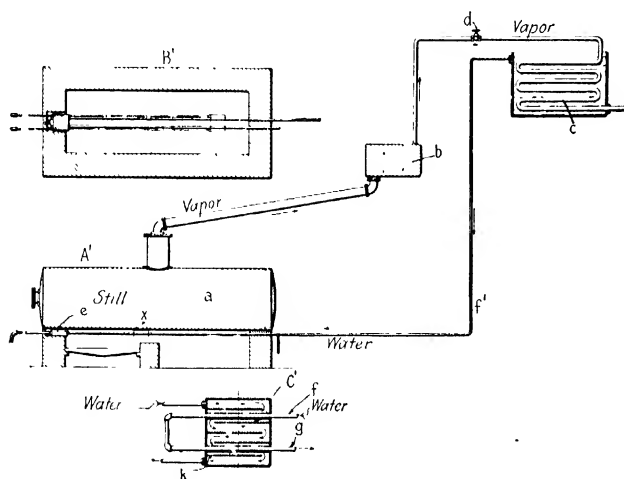
Fig. 93. — Coast pressure still with protective shield.

A large cylindrical cracking still a is arranged above a heating chamber, the latter being provided with a grate. The vapor passing from the still flows through an inclined vapor pipe, then through an air cooled reflux condenser b to a vapor pipe leading to a main condenser c, from which the product is recovered. The condenser is a coil arranged in a water tank.

The apparatus is for use in cracking high boiling point products of distillation. The heavy distillate or residue is introduced into the still, and the desired pressure obtained by regulating a valve d located in the vapor pipe. The pressure in the still and reflux condenser is greater than 50 pounds per square inch, and the temperature of the contents of the still ranges from about 600° F. to 800° F. The low boiling point fractions passing from the liquid flow through the vapor pipe and reflux condenser b to the main condenser c. The relatively high boiling point fractions are condensed in the inclined vapor pipe, or in the condenser b, such fractions being returned to the still through the inclined vapor pipe. This reflux condensate includes a large percentage of heavy, coke forming fractions, mixed with lighter fractions which may be redistilled to form part of the low boiling point product.

A shield e, located in a pocket in the front wall of the heating chamber, is mounted on a horizontal guide consisting of a pair of pipes f and g connected by a shorter pipe h at the front of the still. The pipes f and g, located between the bottom of the still and the fire, are arranged longitudinally. An overflow pipe f' leads from the condenser to the pipe f, the water passing from the condenser being circulated through the pipes f and g. The shield e is a hollow fire proof structure, made of metal and provided with baffles k forming passageways for water, which flows through the shield, and then through a discharge pipe. Sleeves forming part of the shield are loosely fitted to the pipes f and g.

When the still is in service, coke forming fractions settle on the bottom of the still, and at some point a relatively large body of the coke or carbon will accumulate, as indicated by the dotted lines X in Fig. 93. A portion of the still bottom will then be overheated and become red at a point below the coke or carbon. At this time, the operator interposes the shield between the red portion of the still and the heating medium, thereby intercepting the heat so as to protect the coke-covered portion of the still. By protecting the still in this manner, the danger usually due to overheating can be overcome, without cooling the entire still and without removing the coke or carbon. The temperature of the contents of the still is not materially changed, and the cracking operation is said not to be affected.

Another device used by Coast [1] to overcome the difficulty arising from the deposition of coke during cracking is circulation of the oil from one cracking still to another similar one through a trap in which is deposited the coke forming substances. These are then drawn off from the trap.

The object is to remove the coke forming fractions by causing the liquid to overflow from the bottom of one still, through a coke trap and then into another still. The oil to be cracked is forced through a pipe into a still from which it overflows and circulates into the other stills. The different stills are connected together in series. An overflow leads from the lower portion of the still to the lower portion of a trap, and the upper portion of the latter is connected to the second still. The heavy coke forming fractions accumulate at the bottom of the coke trap, and the lighter liquid overflows from the upper portion of the trap and circulates into the second still. A large percentage of the heavy, coke forming substance is thus conducted to the trap, where it will not in any way injure or affect the cracking apparatus. The coke, or tarry, coke forming substance, may be removed from the trap by opening a valve. Figure 94 shows a cross section of a coke trap.

Fig. 94.— Form of coke trap proposed by Coast.

Coast's [2] apparatus for continuously scraping carbon from pressure cracking stills is shown in Fig. 95 which is a vertical sectional view of a still equipped with the device. Scrapers are attached to a longitudinally-moving endless chain C. This is actuated by a gear and

[1] J. S. C. I. 1919, 245A; U. S. Patent 1,291,414, Jan. 14, 1919.
[2] Chem. Abs. 1919, 2276; U. S. Patent 1,307,724, June 24, 1919.

worm. The worm shaft extends through a stuffing box in one of the ends of the shell.

A fused bath of lead is used by Coast [1] in a horizontal pressure still, in order to crack heavy distillates or residues. Molten lead is
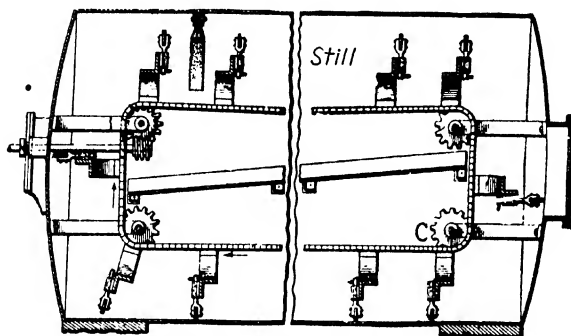
Fig. 95. — Carbon removing device according to Coast.

maintained in the bottom of the still. The oil to be distilled floats upon the surface of the molten lead *A*, Fig. 96, and the heavy coke-forming fractions which drop by gravity to the bottom of the oil also
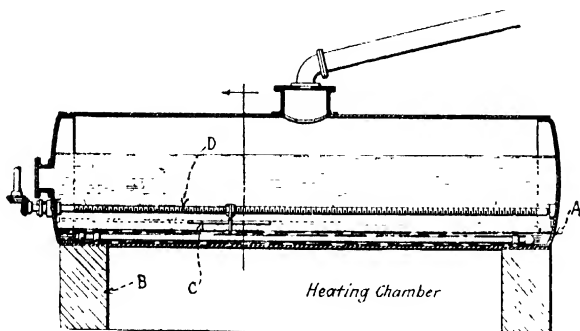
Fig. 96. — Pressure still, with fused lead bath, proposed by Coast.

float upon the lead. The molten lead thus prevents the coke-forming substance from reaching the hot still bottom. The heat is transmitted from the still bottom through the molten lead to the floating oil.

The coke is not a good conductor of heat, and it is, therefore, circulated along the surface of the lead to points directly above the walls *B*, where it will not interfere with the transmission of heat from the heating chamber to the oil. The

[1] U. S. Patents 1,258,190, and 1,258,191, March 5, 1918.

coke is skimmed from the surface of the lead by a skimmer C fitted to a rotary feed screw D which extends through a stuffing box at one end of the still. This feed screw is reversible, so that it may be actuated to reciprocate the skimmer from one end portion of the still to the other. Stationary rods prevent the skimmer from turning on the feed screw. The lower portion of the skimmer extends entirely across the lower portion of the still, and it also extends into the molten lead.

Coast [1] utilizes the heat in the hot exit gases from a tube cracking operation to decompose fresh portions of untreated oil. Oil moving at a high velocity is subjected to considerable heat and the resultant vapors forced into a supplemental cracking chamber. The temperature of the vapors in the supplemental cracking chamber is sufficiently high
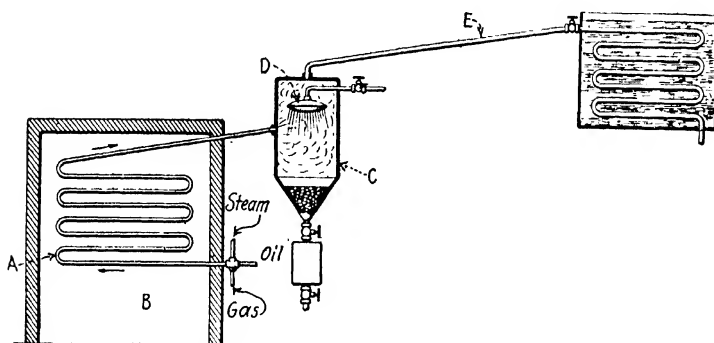
Fig. 97. — Combination of heat exchanger and condenser, in series with a pipe still, according to Coast.

to accomplish cracking and oil in a relatively cool state is introduced into these hot vapors. The result is that the relatively cool liquid, mixing with the hot vapors, causes the vaporized fractions of high boiling point to condense, thus tending to insure a product of relatively low boiling point. The intense heat of the vapors is utilized to crack the liquid oil introduced into the supplemental cracking chamber. Owing to the velocity of the vapors through the cracking tubes, all or almost all of the coke or carbon is forced into the supplemental cracking chamber and is there acted upon by the comparatively cool liquid which condenses the heavier hydrocarbons. (See Fig. 97.)

A coil of pipe A is arranged in a heating chamber B. The coil consists of 400 feet of two-inch pipe. A vapor pipe leads from the coil A to the side of a supplemental cracking chamber C. Another vapor pipe E leads from the top of the supplemental cracking chamber to a condenser. A valve in this vapor

[1] J. S. C. I. 1918, 144; U. S. Patent 1,252,401, January 8, 1918.

pipe is regulated to maintain pressure in the supplemental cracking chamber C and coil A. An outlet attached to the lower end of the supplemental cracking chamber C leads to a receptacle interposed between valves. These valves may be manipulated independently of each other to discharge substances from the bottom of the chamber C without reducing the pressure in it.

A spray is arranged within the supplemental cracking chamber as shown at D. This spray lies above the plane of the vapor inlet and is connected to a supply pipe provided with a regulating valve. Oil is forced through the spray device.

The method is more particularly adapted to crack inexpensive heavy hydrocarbons having a boiling point of about 350° F. to 800° F. (177°–427° C.), the best results being obtained from hydrocarbons having a boiling point ranging from 450° F. to 700° F. (232°–371° C.) The substance to be treated in the cracking coil A is mixed with steam and natural gas, the mixture being pumped into the lower end of the coil. The cracking coil A is subjected to from 800° F. to 1500° F. (427°–816° C.). The velocity of the fluid moving through the cracking coil will range from 2600 to 6000 feet per minute. The valve in the vapor pipe E is regulated to maintain pressure in the cracking coil A and supplemental cracking chamber C. This pressure is between 50 and 150 pounds per square inch.

Relatively high boiling oil is forced through the spray D. This comparatively cool liquid, in a finely divided condition, is discharged into the very hot vapors passing into C. Owing to the intense heat of the vapors, the finely divided liquid is subjected to a cracking operation in the supplemental cracking chamber C. The action in the supplemental cracking chamber will depend primarily upon the temperature of the vapors passing from the cracking coil, the degree of pressure in the supplemental chamber, the boiling points and volume of the oil discharged into it. Only a relatively small volume of oil can be successfully cracked in the supplemental cracking chamber. For example, the quantity of oil forced into the cracking coil may be about five times the quantity forced into the supplemental chamber. The necessary high temperature can be easily maintained in C for, as previously indicated, the vapors passing from the cracking coil are very hot, between 800° F. and 1500° F. (°427–816° C.), and these vapors are discharged at a high velocity into the supplemental cracking chamber

The temperature of the vapors in C is reduced by cool oil passing from the spray D, and as a consequence the vaporized fractions having relatively high boiling points condense and fall to the bottom of the supplemental cracking chamber, instead of passing to the condenser The approximate boiling point and specific gravity of the product may be controlled by regulating the valve to govern the flow of the comparatively cool oil through the spray D, thus regulating the temperature of the contents of C. A product having a desirable low boiling point will, it is claimed, flow constantly from the condenser, the high boiling fractions being condensed in C.

Owing to the high velocity of the fluid passing through the coil A, almost all of the carbon or coke will be carried into the supplemental cracking chamber C, and will fall to the bottom of it. Another method of procedure consists in mixing natural gas with oil and subjecting the mixture to a pressure and temperature sufficiently high to crack the hydrocarbon in the presence of the other elements of the mixture. Coast says that steam and natural gas used with the oil increases the yield and a much sweeter and better product, having a more desirable initial boiling point, is obtained. This seems to indicate that only a very small percent-

age of the oil is converted into a fixed gas, or that portions of the natural gas are absorbed by the oil by the action of steam and heat.

In another method for economizing heat, Coast [1] cracks oil in a still under about 85 lbs. pressure per sq. in. Before entering the still the oil passes through a tank in which vapors from the still are bubbled through the oil layer. Condensed heavier vapors collect in the preheating tank and are returned to the still through an overflow pipe together with fresh oil. Lighter vapors pass up to a reflux condenser and then through a pressure-regulating valve to a main condenser where the lighter vapors are liquefied.

The Use of Natural Gas, Steam and Petroleum Vapors, under Pressure

Cosden and Coast [2] crack oils boiling from 450° F. to 750° F. (232°–399° C.) by means of a retort (liquid-vapor phase) and supplemental vapor retorts. Natural gas and steam are used. Condensation is partly effected by means of cold oil injected into the secondary cracker, so as to utilize, for cracking purposes, a portion of the heat in the vapors from the retort.

The hot vapors resulting from one cracking operation are utilized to heat and crack another oil. To accomplish this, the vapors flowing from a primary cracking chamber are superheated and introduced into a supplemental cracking chamber, and finely divided oil is then forced into the superheated vapors. The injected oil is cracked and, being relatively cool, also serves as a primary condenser for the previously vaporized high boiling hydrocarbons. The high boiling condensate resulting from this operation is conducted back to the primary cracking chamber. By introducing natural gas into the hot vapors passing from the primary cracking chamber the yield and quality of the gasoline produced is said to be increased. The natural gas is heated to a high temperature, about 900° F. (482° C.), and then forced into the hot vapors, superheating them to such a degree that the hot vapor may be used as the heating medium for the second cracking operation. The natural gas is forced into the hot vapors at a point where the vapors are confined under a high pressure, greater than 50 pounds per square inch, and the hot gas is stated to be "absorbed" by the hot petroleum hydrocarbon vapors so as to increase the yield. Before reaching the main condenser, the hot mixture is conducted, under pressure, through a steam chamber where it is mixed with a spray of relatively cool steam.

[1] Chem. Abs. 1920, 1436; U. S. Patent 1,333,964, Mar. 16, 1920.

[2] J. S. C. I., 1918, 405A; Chem. Abs., 1918, 1597; U. S. Patents 1,261,215, Apr. 2, 1918; 1,258,196, Mar. 5, 1918.

This causes some of the high boiling hydrocarbons to condense, and the properties of the product are believed to be improved by the action of the steam It appears, according to the investigators, that some of the constituents of the steam unite with the hydrocarbons so as to form part of the low boiling product. The steam is also said to obviate a large percentage of the carbon that is usually removed by treating the product with sulphuric acid.

A retort *A* (Fig 98) is arranged over a heating chamber. A vapor pipe *B* leads from the retort to a supplemental cracking chamber *C*. A vapor pipe *D* connects the upper portion of the supplemental cracking chamber to the steam
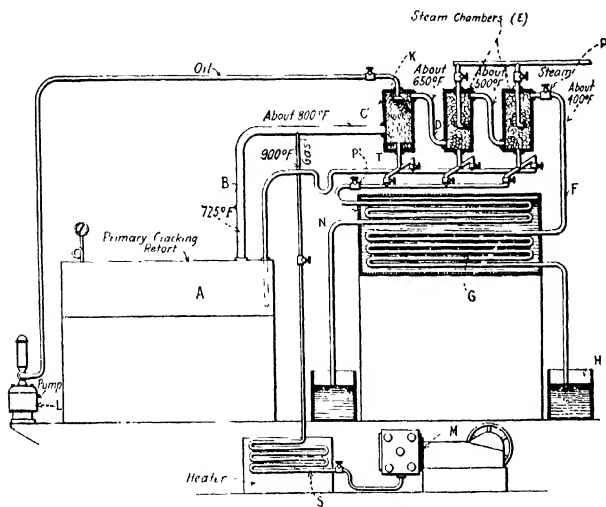
Fig. 98. — Diagram showing method of cracking oil in the presence of steam and natural gas, according to Cosden and Coast.

chambers *E*. A vapor pipe *F* leads from the upper portion of the second steam chamber to a main condenser *G*. A nozzle *K* arranged in the upper portion of the supplemental cracking chamber discharges a finely divided liquid hydrocarbon into the hot vapors. A pump *L* forces a high boiling hydrocarbon liquid to the nozzle *K*. Natural gas passing from a gas compressor *M* is forced through a superheater and then into the insulated vapor pipe *B*. The condensate forming in the supplementary cracking or steam chambers may be returned to the main cracking chamber *A* or it may be conducted to a cooling coil *N*.

A pressure regulating valve *P* in the vapor pipe *F* may be adjusted to maintain any desired pressure in the steam chambers, supplemental cracking chamber and main cracking chamber. A regulating valve *P'* is also adjusted to maintain the desired pressure when the condensate flows to the coil *N*.

The method may be used, it is stated, in cracking various high boiling hydro-
carbon products resulting from the distillation of crude petroleum, and in cracking
a variety of heavy hydrocarbons having a boiling point of about 450° F. to 700° F.
(232°–371° C.). The substances to be treated are introduced into the main crack-
ing chamber, and the valve P located beyond the steam chambers is adjusted to
maintain the desired high pressure in the steam chambers and cracking chambers.
This pressure is about 75 to 80 pounds per square inch.

The vapors flowing in the vapor pipe are superheated by the natural gas
flowing from the heater S and the hot mixture is then conducted into the supple-
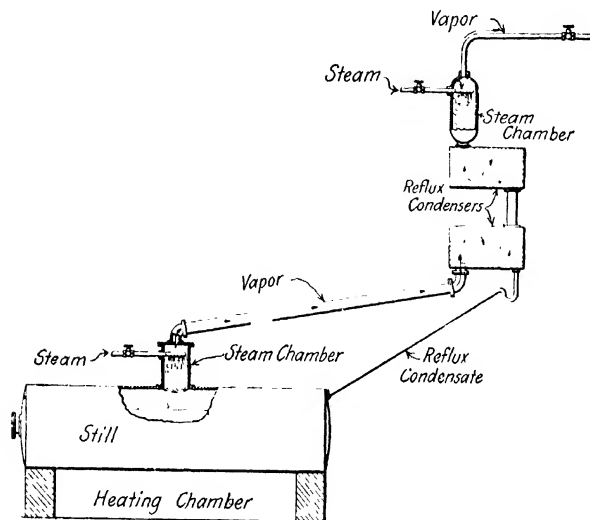
Fig. 99. — Pressure still, with reflux condensers, showing use of "top" steam.

mental cracking chamber. The natural gas under pressure and at a high tempera-
ture, about 900° F. (482° C.), mixes with the confined vapors, so as to increase the
yield, at the same time increasing the temperature of the vapors to such a degree
(for example 800° F. (427° C.)) that the mixture serves as a heating medium for
cracking the high boiling hydrocarbon oil passing from the nozzle in the supple-
mental cracking chamber. The finely divided oil discharged into this chamber
is a high boiling product. It should be in a liquid state and at about the
temperature of the atmosphere. This high boiling fluid is vaporized and cracked
while confined under pressure in the supplemental cracking chamber, and it also
serves for condensing previously vaporized high boiling fractions. The elimination
of coke or carbon by the action of the relatively cool liquid in the supplemental
cracking chamber is stated to be accomplished. A large percentage of the carbon
or coke carried by the vapors drops into a trap formed at the bottom of the sup-
plemental cracking chamber, and the high boiling condensate overflowing into the
discharge pipe T is conducted back to the primary cracking chamber A.

The Use of "Open" Steam for Separating Heavy from Light Hydrocarbons. — Petroleum hydrocarbons of high boiling point, according to Coast,[1] e.g., oils boiling 230°–370° C. (446°–698° F.) are vaporized and cracked under a pressure of 50–150 pounds per square inch and steam of a somewhat lower temperature than the hydrocarbon vapors is introduced into the latter above the liquid level in the retort. This treatment causes the vapors of hydrocarbons of relatively high boiling point to condense and return for further cracking treatment while the lighter hydrocarbon vapors are led off and condensed. The main condenser is operated under about atmospheric pressure and the retort, air-cooled condenser and steam chamber are maintained under a pressure of about 80 pounds. Fig. 99 shows the apparatus used.

Fig. 101. — Still provided with false bottom.

Other Methods of protecting Still Bottoms. In Fig. 100 is shown an elaboration of Coast's method for protecting still bottoms by means of fused lead. In this particular process [2] lead is constantly circulated from the lowest portion of the still and brought
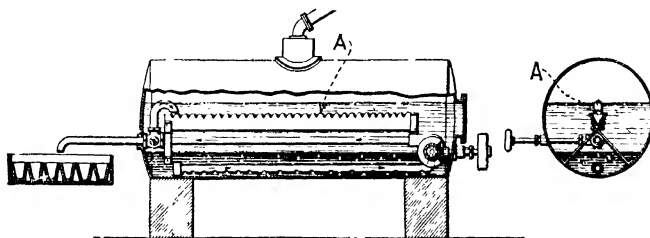
Fig. 100. — Use of fused lead on bottom of pressure still, with means for circulating the lead, according to Coast.

into contact with the upper strata of oil by means of the distributing device *A*, Figs. 100 and 101.

Another and radically different method of preventing the formation of hard carbon deposits on the bottom of cracking stills [3] consists in the maintaining of a false bottom and causing oil to circulate rapidly

[1] Chem. Abs. 1918, 531; U. S. Patents 1,250,798, 1,250,799, and 1,250,800, Dec. 18, 1917.

[2] U. S. Patent 1,345,134, June 29, 1920.

[3] U. S. Patent 1,345,133, June 29, 1920.

between the still bottom proper and the false bottom by means of blasts of gas. In Fig. 101 is shown the false bottom and delivery pipes for admitting gas under pressure to the space between the bottom of the still and the false bottom. The gas used may be refinery still gases produced in cracking.[1]

[1] See also U. S. Patent 1,345,132, June 29, 1920.

CHAPTER XII

CRACKING HEAVY OILS IN THE LIQUID STATE OR PHASE

Liquid Phase High Pressure Methods

Tube and Retort Cracking. Liquid Phase. — This chapter deals with those processes in which tubes or retorts play an essential part. The strictly liquid phase processes are not numerous. The range of temperatures necessary for cracking hydrocarbons, in general, are above the critical temperature of many light hydrocarbons, such as those found in naphtha, solvent oils, and illuminating oils. It is possible, as in the processes of Testelin and Renard, Fenchelle and Perkin and other methods to maintain such a high externally applied pressure that the tendency of the lighter oils to volatilize is overcome, but the pressures necessary are very high, 40–60 atmospheres, for example. The processes considered here include therefore those where it is thought the cracking in the liquid phase is at least as vital or noteworthy a part of the process as the decompositions in the vapor phase.

It will be noted that even though the cracking temperatures are above the range of critical temperatures of many of the lighter hydrocarbons, nevertheless, the vapor pressure of these substances (e.g., pentane, hexane, hexylene, etc.) is very much lowered by the fact that they are in solution in a fairly large body of heavy hydrocarbon oil. With sufficient pressure, therefore, it is possible to maintain a liquid phase in decomposing heavy oils even though the temperatures employed are above the critical temperatures of some of the hydrocarbons produced by decomposition.

The cracking of petroleum in the liquid phase is discussed by **R. Cross,**[1] who recommends applying heat to the petroleum in the liquid phase, maintaining a pressure of about 30 atmospheres and a temperature of not more than 400° C. (752° F.). The advantages of this method over cracking in the vapor phase are stated to be (1) greater yield and better quality of the product; (2) selective action on the heavy hydrocarbons; (3) the gasoline is removed from the reaction zone as fast as it is formed; (4) high heat economy; (5) carbon is deposited in the suspended condition and not on the walls of the tubes;

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[1] J. S. C. I. 1917, 860; Met. and Chem. Eng. 1917, 643–645.

(6) high oil capacity with small plant; (7) perfect temperature control; (8) rapid and complete absorption of heat from the furnace, and (9) convenient continuous or intermittent working of the process. The only serious disadvantage is the high pressure required with possible danger of explosive destruction of the apparatus.

Testelin and **Renard** [1] describe a process which is an excellent example of a clearly cut one-phase tube-cracking method. Figure 102 shows a diagrammatic view of the apparatus. The outstanding features of the apparatus are the coils E and F. They are practically identical and are constructed of very thick-walled steel tubing. For example, they may be 10 mm. internal, 20 mm. external, diameter, with a total length of ten meters. Such an arrangement presents a large heating surface per unit volume of confined liquid. The investigators state that this ratio in their described apparatus is represented by one square meter for each 1177 cubic centimeters volume of confined liquid. Coil E is immersed in a bath of fused lead, whereas the liquid surrounding F is water. In other words, E is the reaction chamber and F the condenser. A is a force pump, B a recoil modifier, C an air chamber, and G a pressure reducing valve.

Fig. 102. — Testelin and Renard's liquid state cracking method.

The process is carried out as follows: the pump A is set in motion and the valve G vented in order to fill the apparatus with petroleum and drive out all air. The valve G is then adjusted, so that the pressure gage D indicates about forty atmospheres (600 pounds per square inch). The temperature of the lead bath is then brought to 400°–450° C. (752°–842° F.) and oil continuously forced through the apparatus. The pump A and the valve G constantly maintain the oil at pressures in excess of the vapor pressure of the constituents of the oil, so that there is no vapor, as such, produced in the coils. It is not stated that any gummy or carbonaceous matter is formed in the coils. It is, however, pointed out that petroleum treated by this process, if allowed to stand several weeks, deposits a heavy tarry or resinous mass; that the density of the supernatant liquid simultaneously decreases

[1] German Patent 226,958, May 13, 1909.

corresponding to the degree of its clarification; and that this upper
layer finally becomes quite clear.

See also British Patent 3413, Feb. 10, 1913.

Fenchelle and **Perkin** [1] convert heavy hydrocarbons into lighter
products by heating them in the liquid state to 500°–600° C. (932°–
1112° F.) under a pressure of 50–60 atmospheres. The liquid, still
under pressure, is then cooled to about 150° C. (302° F.) and allowed
to escape at a lower temperature into a chamber in which the lower
hydrocarbons vaporize simultaneously.

 Perkin (*ibid*), in discussing his process, states that the pressure on the oil is
always so high that the oil never reaches its critical temperature and never there-
fore passes into the form of vapor. This feature reduces the amount of free car-
bon deposited. But, as in other processes, gummy dienes and trienes are formed
and although they may be removed, e g, by sulphuric acid, there may be the pos-
sibility of their reformation.

 Lucas (*ibid*), referring to Perkins's discussion, states that he believes an
olefin formed in the process of cracking from paraffin oil may repeatedly break
up and reform again before it takes its final form. If that were so, the rate at
which it is cooled after breaking up the original oil must have a great influence on
the final product, it is said. He has found by actual experiment that if gases are
allowed to remain at a certain temperature for a considerable period, and cooled
slowly, the products are quite different in many respects from those which would
be obtained with sudden cooling; in other words, sudden expansion after heating
gives, it is stated, totally different results from those obtainable by cooling at the
same pressure as the vapor issues from the cracking tube.

This process of **Fenchelle** and **Perkin** [2] is carried out by pumping
heavy oil or heavier raw material (kerosene, naphthalene or paraffin dis-
tillate) through pipes heated to 500°–600° C. and under a pressure of
50 60 atmospheres. Thus, the pressure is so high that although the
temperature exceeds the critical temperature of some of the hydro-
carbons produced, nevertheless they remain dissolved in the main body
of liquid hydrocarbons present. This is one of the few examples of a
true "liquid phase cracking process." It is important to note that
these investigators cool and partly condense under high pressure; that
is, the same pressure that exists in the cracking tubes, less the decrease
due to the reduction of pressure in cooling. In Fig. 103, A is a heating
chamber or furnace enclosing a number of nests of tubes the ends of
which are supported in the furnace walls and are so connected together
as to constitute a long narrow conduit. The tubes are arranged in
two sets, A^1 and A^2; one set A^1 being of fairly large bore for preheating

 [1] The "Pyrogenesis of Hydrocarbons" by **Lomax, Dunstan** and **Thole**, Journ.
Inst. Petroleum Technologists, 1916 (3), 36; British Patent 6547, Mar. 14, 1914.

 [2] J. S. C. I. 1915, 415, British Patent 6547, March 14, 1914.

purposes and the other set A^2 of small bore for the actual cracking
operation, the preheating tubes A^1 being arranged in the upper part of
the cracking chamber so as to be heated by the hot air and gases rising
from the lower part of the chamber where the more intensely heated
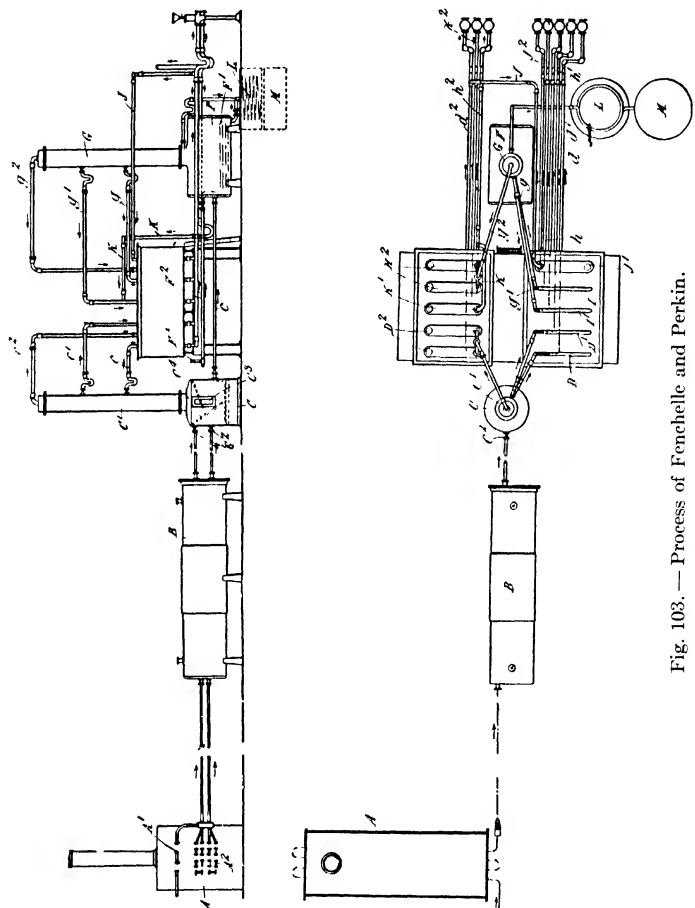
Fig. 103. — Process of Fenchelle and Perkin.

cracking tubes A^2 are arranged.   A force pump (not shown) is employed
to drive the heavy hydrocarbon oil or liquefied solid hydrocarbon from
a supply tank through the preheating tubes and through the cracking
tubes proper at a pressure of from 50 to 60 atmospheres, the tubes
being sufficiently strong to safely withstand this pressure.   The tubes

are straight and open ended, the ends projecting beyond the chamber walls and being connected by detachable bends, so that individual tubes may be easily inspected and cleaned at any time but constitute a long continuous conduit when in use. Each preheating tube A^1 may be arranged to supply a nest of, say, four cracking tubes, and the whole system of connections, including the necessary valves, is such that a small portion of the tubular arrangement can be thrown out of action without interfering with the action of the remainder.

The hot oil proceeding from the cracking chamber A at a temperature of about 500° to 600° C. (932°–1112° F.) gives up some of its heat to the water in a boiler B by passing through a nest or nests of tubes therein, a lift valve being provided on the boiler so that a constant steam pressure can be maintained, thus enabling the temperature to which the oil is cooled in the boiler to be readily maintained and regulated. If, for example, it is desired to cool the oil to 150° C. (302° F.), the steam pressure in the boiler should be kept at about sixty pounds per square inch. The cracked and partially cooled oil proceeds from the boiler B through tubes to a chamber C at the foot of a dephlegmator or rectifying column C^1. The pressure in this chamber C is about atmospheric, so that the oil, after passing through valves C^2 for maintaining the desired pressure in all the tubular passages extending from the force pump to this chamber is suddenly relieved of pressure, the result being that any occluded gases and all volatile constituents having a natural boiling point below the temperature of this chamber separate out from the unconverted or " uncracked " oil and pass out of the chamber C into the dephlegmator or rectifying column C^1.

In order to watch the flow of the cracked and partially cooled oil into the separating chamber C, a window C^3 is provided, and, in order that the sudden ebullition of the oil as it enters the separating chamber may not give rise to entrainment, one (or more) slanting baffle plate C^4 is provided near the oil orifices to direct the oil to the bottom of the chamber.

The gases and lighter hydrocarbons spontaneously liberated from the heavier and uncracked oil pass up the dephlegmator or rectifying column C^1, from which they issue at various heights and pass by way of pipes, c, c^1, c^2, into condenser coils, D, D^1, D^2 from which the products of condensation, namely hydrocarbon oils of relatively low specific gravity and boiling point, are run into receiving or storage tanks. The lightest portion of the vapors, namely that traversing the pipe c^2, coil D^2, and pipe d^2 may not be entirely condensed, and any uncondensed fraction is passed into a condenser coil J^1, and thence by way of a pipe J^2 to a storage tank (not shown). The heavier or uncracked liquid remaining in the separating chamber C at the foot of the dephlegmator or rectifying column C^1 is run off through a pipe c and passed into a still F, which is connected with a second dephlegmator or rectifying column G, and the vapors ascending this column are carried off at different heights or levels by way of pipes g, g^1, g^2, to separate condenser

coils H, H^1, H^2, from which the condensation products are run through pipes h, h^1, h^2 into separate receiving or storage tanks (not shown). The lightest portion of the vapors, namely that traversing the pipe g^2 and condenser H^2, may not be entirely condensed, and any uncondensed fraction leaving the condenser through the pipe h^2 is passed into a condenser coil K^1 and then to a storage tank. Any uncondensed gases or vapors may be led to a scrubbing and washing plant and then to a gasometer, and eventually used as fuel.

In order to heat the still F, steam is passed through the piping $F^x F^2$ to a coil F^1 in the still, the steam being obtained from the boiler B, and the steam or water issuing from the coil F^1 being led to a steam trap. The liquid collecting at the foot of the dephlegmator G, and the residue in the still F, is drawn off into a cooler L and then into a tank M, from which it is returned to the supply tank of the cracking chamber, fresh heavy oil or liquefied solid hydrocarbon being added to this tank from time to time so as to keep the level constant and thus render the whole process a continuous one. The various tubes or nests of tubes are provided with inlet and outlet valves and these valves are such as will resist the effects of the high temperatures and pressures to which they may be subjected.

A process which was apparently intended to utilize light " cracked " or unsaturated hydrocarbons as a means of " saturating " the heavier unsaturated oils is described by **G. L. Benton**.[1] It is specifically stated that the object was to avoid the production of gasoline (or benzine, as it was then more frequently called), and to increase the production of illuminating oils. The oil is heated to high pressures (about five hundred pounds) and high temperatures [e.g., 700° F. (371° C.)] and then released or expanded into a heated chamber at atmospheric pressure. Crude oil is used directly.

In the chamber-space f is arranged the coiled pipe B, Fig. 104, connected at the rear end through the furnace wall with the oil supply, and provided at this end with a pressure gage, S. This pipe extends at the front end through the furnace wall, and is provided with a pyrometer, P. The pipe B is continued up into the vapor chamber C, as shown, and this end of the pipe B is provided with a rose or perforated cap, through which the highly heated crude oil can be sprayed into the chamber C.

The vapor chamber C is an inclosed metallic vessel. It is fitted into the top of the furnace and has a dished bottom, which is exposed to the heat of the furnace f, and it has an outlet pipe, h, leading off through the furnace to the outside. Underneath the top of this vapor chamber C, and above the spray-pipe B, is a deflecting-hood, m, extending out toward the sides of the chamber, but having an annular space between the edge of the hood and the side of the vapor chamber. In the top of the vapor-chamber is a pipe which leads off to the manifold H, which is a condensing-box of the ordinary construction, and then by pipes to the condenser D, or the vapor may pass directly from the chamber C to the condenser D. A stop cock, g, is arranged to be operated from the outside of the vapor chamber, to regulate the discharge of the highly heated oil from the pipe B into the chamber C, or to confine it to the pipe B.

[1] U. S. Patent 342,564, May 25, 1886

Operation is conducted as follows: The stop cock *g* being shut and the waste-pipe *i*, connected with the pipe *B*, being opened, a fire is started on the grate *a*, and the crude oil is let in from the supply to the pipe coil *B* and allowed to flow out through the waste pipe *i* (from which it is led back to the supply), while the pipe *B* and the chamber *f* attain the proper temperature.

When the furnace has attained the proper temperature, the waste pipe *i* is closed and the stop cock *g* being already shut the oil is thus confined in the pipe *B* under the pressure of the supply pump, which feeds the oil.   The oil with which the pipe *B* is thus filled is kept under this pressure until the pyrometer indicates that it has attained a tem-
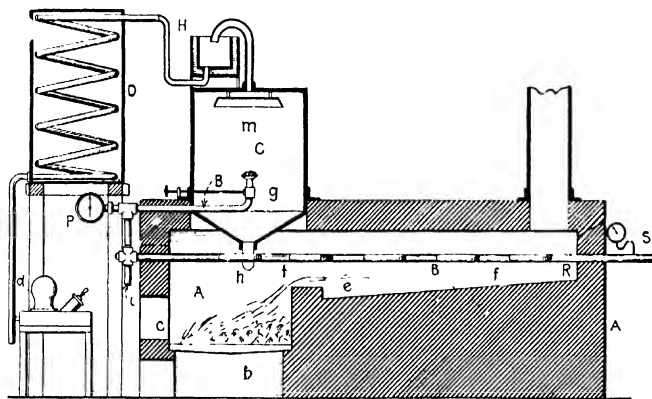
Fig. 104. — Pressure pipe still according to Benton.

perature sufficiently high to have had a "latent vaporizing effect" upon the oil (this temperature ranges from 700° to 1000° F. (371°–538° C.)) when the stop cock *q* is opened and the released vaporized oil rushes out through the rose in the end of pipe *B* and strikes on the under side of the hood *m*, from which it is deflected downward, and then rises through the annular space between the hood and the wall of the chamber *C*, and passes into the pipe which leads directly to the condenser *D* or to the manifold *H*, and then by pipes to the condenser *D*, and through this condenser into a receiving tank. The chamber *C* will have become heated before the admission of the vaporized oil into it, and its temperature is maintained by the furnace to correspond with that of the spray escaping into it from the coiled pipe *B*, through which the passage of the crude oil is now kept up continually under the regulated pressure at such velocity to provide time for its required increase of temperature while passing through the furnace.

To promote the passage of the vapor from the chamber *C* to the condenser *D*, an ordinary air-pump is connected with the lower end of the coil *D* at *d*. The oil is raised to and maintained at a sufficiently high temperature to vaporize it as soon as it is released from the pressure under which it is confined in the pipe *B*, while, until so released, it is prevented by the pressure from vaporizing at all, and, consequently, when it is permitted to escape into the heated chamber *C* it bursts into vapor. This is deflected in the chamber *C* and then passes off into the condenser *D*, while depositing heavy products in the bottom of the chamber *C*. These are drawn off through the pipe *h* in the bottom of the chamber *C*.

R. R. Rosenbaum[1] heats liquid hydrocarbons under pressure to a temperature considerably above their normal boiling point and the
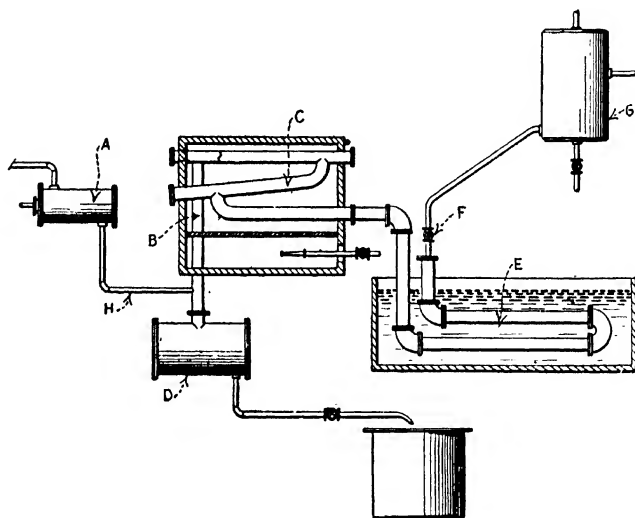
Fig. 105. — Pressure pipe still provided with tar or carbon pot, according to A. R. Jones.

highly heated liquid is then discharged into another chamber, where it is allowed to vaporize and expand to effect partial decomposition into lighter hydrocarbons. Petroleum oil may be directly treated by this method or may be subjected to a preliminary distillation and dephlegmation and selected condensates then subjected to superheating and cracking. An increase of about 50 per cent in the yields of gasoline and naphtha are asserted to be obtainable.

A. P. Bjerregaard[2] has made a study of the cracking of various heavy oils at high pressures and temperatures. The pressures used

[1] Chem. Abs. 1920, 465; U. S. Patent 1,324,983, Dec. 16, 1919.
[2] J. Ind. Eng. Chem. 1915, 573.

ranged from 275 to 1400 pounds per square inch and the temperatures from 350° to 440° C. (662°-824° F.).   No aromatic hydrocarbons were formed.   Above 400° C. (752° F.) the yield of gasoline (oils boiling below 150° C. (302° F.)) appeared according to Bjerregaard to rapidly diminish, even though the pressure was increased from 400 up to 1400 pounds per square inch.   A tubular cracking arrangement was used.

A. R. Jones [1] arranges a pipe still in series with a condenser coil, the latter being in free communication with the pipe still. Fig. 105 shows
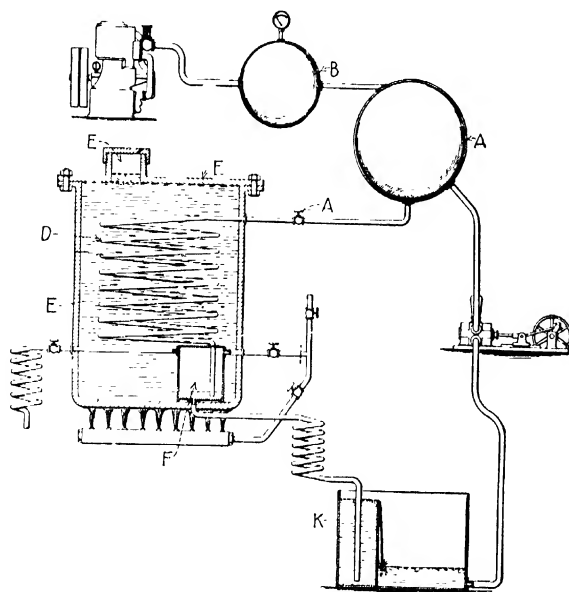
Fig. 106. - Kittle's process.

the arrangement. *A* is a force pump, *C* the pipe still, *E* the condenser, *F* a throttle valve and *G* a dephlegmator.   Fig. 105 is a vertical view partly in section.   Attention is called to the pipe *B* which is in free communication with a closed reservoir *D*.   Since the feed pipe *H* is of small diameter as compared with that of *B*, the flow of oil through the pipe still is said to be very- slow and on this account there is a good opportunity for carbon formed in *B* to settle out and fall into the reservoir *D*.   The apparatus may be operated up to 20 atmospheres as an upper limit although ordinary operation pressure is about 100 pounds to the square inch.

[1] U. S. Patent 1,328,522, Jan. 20, 1920.

H. A. Kittle [1] pumps oil through a twenty-foot length of very small pipe (3/16″ diameter) under a constant head of pressure (100 pounds). Emphasis is laid on the fact that the velocity of flow of oil is greater than that velocity with which a drop of the oil would spread, if dropped on to a hot surface, at a temperature higher than the boiling point of the highest boiling constituent. The apparatus is shown in Fig. 106. *B* is a compressed air chamber, *A* an oil reservoir, *E* a vessel containing molten metal, *D* the vaporizing and cracking coil, *F* an expansion chamber, *K* a reservoir for unconverted oil. Evidently the pressure in the coil is not sufficient to keep the reacting bodies and products in the liquid state; nevertheless, the velocity of flow of oil is maintained higher than that at which a film of the oil would spread on the surface of the coil, hence undue superheating of the vapors is apparently avoided.

Liquid-Vapor Methods

In an apparatus for cracking oils, described by **Lambert** [2] a heating pipe which is coated with heat insulating material and contains electric heaters passes through a still chamber. A pump within the chamber forces the oil under high pressure through the heating pipe to a series of branch pipes in the upper part of the chamber. The heated oil is sprayed from these pipes by detachable sprayers into the vapor space, and the gaseous products are withdrawn. Heavy condensed oil is returned to the still and the lighter vapor then condensed.
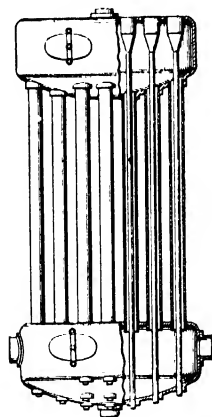
Fig. 107. — Method of Johnson and Snodgrass.

Johnson and **Snodgrass** [3] have devised a cracking apparatus, one of the features of which is a unit that, as shown in Fig. 107, is made up of a number of vertical tubes provided with top and bottom drums or headers. The method is intended for the cracking of petroleum residues or pitches. A battery of these units is employed in conjunction with ordinary stills. The tubes receive direct fire. They are fed by gravity, from the stills, with heavy residues which are preheated with the waste gases from the main furnace setting, in which the units referred to are located. The generated vapors are collected in a vapor reservoir. A deposit drum is located

[1] British Patent 8336, Apr. 6, 1909.
[2] J. S. C. I. 1918, 4A; United States Patent 1,245,930, Nov. 6, 1917.
[3] U. S. Patent 1,283,202, Oct. 29, 1918.

below the several drums of the units and communicates with them.
The vapors from the reservoir collect in a drum from which a dephleg-
mator or runback inclines upwardly for carrying the vapors to the
condenser.   The drum is provided with a safety valve to relieve exces-
sive pressure.

A rather novel scheme for a continuous cracking process has been
devised by **Trumble.**[1]   In the general aspects of his apparatus, he
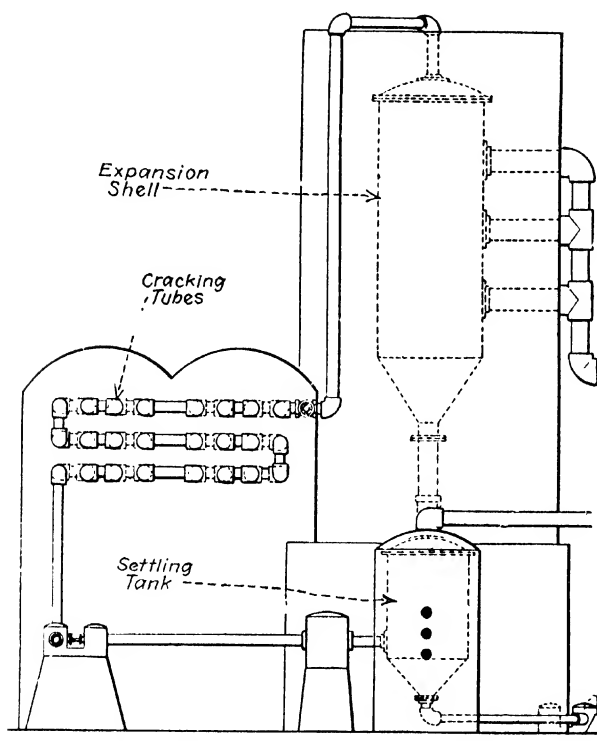
Fig. 108. — Trumble's pipe still with separating drum.

combines (*a*) horizontal cracking tubes with (*b*) a vertical cylindrical
expansion shell and (*c*) a settling tank located directly beneath the
expansion shell.   The expansion shell is exposed to the hot gases from
the furnace in which the tubes are located.   Oils which are condensed
in the expansion shell run into the settling tank and are for the most

[1] Chem. Abs. 1917, 1039; 1919, 185; J. S. C. I. 1916, 1210; United States
Patent 1,281,884, Oct. 15, 1918; British Patent 15,084, Oct. 25, 1915.

part returned to the cracking tubes. However, portions of the resid-
ual oils in the settling tank are removed, together with tarry and
carbonaceous matter, and are used as fuel. This feature, it is stated,
prevents an accumulation of carbonaceous and other undesirable
matter in the system. Fresh oil is constantly supplied to the cracking
tubes and vapors constantly emerge from the expansion chamber.
The oil is rapidly circulated through the heating oils under pressure or
not, as desired. It is stated that, due to the evolution of vapor, an
emulsion of vapor and oil is produced in the coils. It therefore passes
into the expansion chamber in the form of a foam, in which baffles
cause the foam to separate into vapor and heavy oil. The heavy oil
flows by gravity to the settling tank and the vapor is removed from the
expansion chamber. (See Fig. 108.)

It is stated that the essential features may be summed up as follows:

1. The forcing of heavy oils through a heating coil, heated to a sufficient
degree to crack the oil, at such a rate and at such a pressure that the oil can be
changed into a foam without danger of unduly heating or burning the oil.

2. The immediate release of the foam, the removal of vapors from the foam
and the immediate recirculation and reheating of the oil to form more foam, keep-
ing the oil in continuous motion over a closed ring or path.

3. The condensation of a portion of the vapors, and the return to the coil of
the heavy distillate. The use of a settling tank and the continuous removal of
heavy oil and foreign matter from the bottom of this tank, so that accumulations
of solid matter are prevented and the composition of the oil is maintained constant.

Higgins [1] renders heavy hydrocarbons suitable for use as motor
spirit by passage through a retort pipe of undulating form having
bends in which the liquid is held during heating. The heavy oil is
supplied slowly and is more or less vaporized in the first bend and
again subjected to heat in the second bend. The resulting vapors
pass to a condenser. Among the hydrocarbons thus treated are crude
naphtha, crude tar oil, shale oil, and paraffin oil.

The Simplex Refining Company [2] circulates heavy oil, with or with-
out pressure, in a continuous cycle, e.g., through serpentine tubes,
which are heated to the " cracking " point of the oil. The resulting
vapor is continuously removed and fresh oil added to keep the circu-
lating oil at a constant volume. A portion of the condensed light
vapor is injected into the residue when it returns to the heating vessel.
The advantages of this process are stated to be regularity in working
and the prevention of overheating and formation of carbonaceous and
viscous deposits within the tubes.

[1] J. S. C. I. 1916, 919; Chem. Abs. 1917, 98; British Patent 9418, 1915.
[2] J. S. C. I. 1917, 127; French Patent 480,147, June 22, 1916; Danish Patent
21,511, Sept. 18, 1916.

A process which does not involve circulation of the main body of oil while being cracked is described by **Bacon, Brooks** and **Clark.**[1] The method utilizes mineral oils whose boiling point is 250° C. (482° F.) and upward, for the production of a mixture of hydrocarbons principally of the C_nH_{2n+2} series, boiling below 200° C. (392° F.). The mineral oils from which the product is obtained are petroleum hydrocarbons, for instance, American and Mexican petroleums. The operation is conducted at a pressure of from 60 pounds to 300 pounds per square inch, and at a temperature of from 350° C. to 500° C. (662°–932° F.). The method is designed to avoid the difficulty of carbon deposit by conducting the operation under such conditions that the particles of tar and coke produced in the mass will tend to move out of the cracking zone of the still and deposit themselves in a part of the apparatus separate from it.

While the production of the desired product depends upon the maintenance of high temperatures and high pressures, the rate of production is a function of the area of heating surface employed and, for most purposes, may be regarded as represented by the ratio of the heating surface to the volume of the oil within the heating space. Accordingly, it is found that the maximum yields, in a given unit of time, from a given volume of oil heated, are obtained when the ratio of the heating surface to the volume is correspondingly large. In practice, tubes of an internal diameter as large as 19 inches (corresponding to a ratio expressed in comparable units, of internal surface to internal capacity of 1 4.7) have been employed, this numerical ratio being derived when the inch is taken as the unit of measurement. The employment of tubes of materially large diameter, because of the rapidly decreasing yield in gasoline beyond that point, is not advised.

The particles of tar and coke that are formed during the operation move out and deposit in a part of the apparatus separate from the heated surfaces which effect the cracking of the oil. The still is constructed in such a manner that its heating zone is upright and is a portion of a tube of small diameter with respect to its length. The tube is supplied with the oil by a pump discharging into its upper portion. At its lower end the tube leads into a receptacle for the collection of the tar and coke particles. The arrangement is such that the receptacle in which the tar and coke are received is entirely below the heating zone of the tube, so that the particles of tar and coke will fall freely through the oil column into the collecting space below. Whatever tar and coke is deposited upon the upright walls of the heating zone is relatively small in amount, so that the cleaning of the tube to remove these accretions is not frequently required.

Another characteristic of this method is that the danger of explosions is lessened at the pressures employed, because of the much larger resistivity to pressure incident to the employment of small tubes as compared with the employment of a single large still, either of the horizontal or vertical type.

In Fig. 109 is shown a single unit consisting of a tube *b*, of steel whose length is 20 ft. or more, when the internal diameter of the tube is 6 inches. The heating zone of the tube is between its ends and consists of a fire brick chamber *C* having

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[1] Chem. Abs. 1915, 1113; United States Patent 1,131,309, Mar. 9, 1915.

air inlets *d* and opening *e*, for the products of combustion. The chamber *C* receives its heat from a series of annular gas burners *f*, supplied with a mixture of air and gas from the gas conduit *D*. At its lower end the tube *b* communicates with a tar and coke receiving receptacle *E*, located below, outside of the heating zone. At the beginning of the operation, the charge of oil to be cracked and distilled is established up to the level indicated; that is to say, at a level slightly higher than the internal wall of the top of the heating chamber *C*. This level is kept practically constant, by means of a pump which supplies oil to the interior of the tube. Accordingly, the products of combustion

do not come into direct contact with any portions of the tube not occupied by the liquid oil, and consequently the danger of destructive distillation of any portion of the vapors by coming into contact with overheated portions of the tube above the zone of liquid oil is minimized and the formation of an adhering layer of coke upon portions of the walls of the tube is avoided. The free portion of the tube extends above the furnace setting for a distance of about 5 feet. The vapors pass through the pipe *i* to a condenser coil. At the bottom of the receptacle *E* a pipe conveys the residual tar and coke to a receiving tank.

In carrying out the process, the receptacle *E* and the tube *B* are filled to the level indicated, and the annular burners *f* are lighted. The temperature rises from 350° to 500° C. (662° 932° F.) and the pressure is permitted to rise until the pressure gage *t* indicates a pressure of about 100 pounds. At 100 pounds pressure about 75 to 90 per cent of the entire body of oil may be distilled with the production of a resultant condensate containing a large percentage of material boiling below 200° C. (392° F.), the temperature being about 425° C. (797° F.). About 35 per cent of the condensate obtained at this

Fig. 109. — Vertical still with "sump" for removal of tar and carbon, according to Bacon, Brooks and Clark.

pressure and temperature has a boiling point below 150° C. (302° F.) and almost all of this product is of the paraffin series. It is preferred to operate at a pressure of 100 pounds for the reason that the relative portion of the material boiling below 150°

C. (302° F.) is greater when the operation is conducted at 100 pounds pressure than when conducted at the lower pressure of 60 pounds per square inch. The higher pressures up to 300 pounds are employed when it is desired to still further increase the relative proportion of material in the condensate boiling below 150° C. (302° F.), but at the higher pressures there is progressively more coke and gas formed and hence a lower percentage of total condensate is obtained.

During the cracking and distilling operation, any particles of tar and coke that may be formed in the body of the oil tend to fall through the vertical heating zone, by gravity, into the receiving space of the chamber *E*. A relatively small amount of tar and coke builds up upon the vertical walls of the tube *B* within the heating zone, but these accumulations are relatively unimportant, it is said, and slow of formation, and may be readily removed by the use of any or-

dinary boiler flue cleaner. The petroleum residue containing the coke accumulating in the receptacle E is drawn off from time to time through a pipe into a receiver.

Suckert [1] has proposed simultaneously to desulphurize and crack petroleum oils by passing them in contact with a desulphurizing substance (oxides of copper, lead, calcium and iron) under a pressure of from one hundred and fifty to two hundred pounds per square inch and a temperature ranging between 500° and 600° C. (932°–1112° F.), through a coil of the type shown at O in Fig. 110 and then through a mass of the oxides named, shown at R. After subsequent expansion the oil is distilled. In addition to desulphurization, light oils and permanent gas are produced.

An intermittent process in which kerosene or heavier oil circulates back and forth between a series of cracking tubes and a horizontal cylindrical converter is proposed by **W. M. Cross**. [2] Referring to Fig. 111 heat

Fig. 110. — Pipe still in series with desulphurizing chamber, proposed by Suckert.

is applied to the oil in tubes a which are located in furnace setting s. Pump c, actuated by motor f, constantly circulates oil through the tubes, from these to the converter and back through the tubes. No external heat is applied to the converter for cracking purposes. When cracking has proceeded far enough, the charge is drawn off from b and distilled to recover light oils.

If the converter tank b is partially filled with gasoline and the temperature raised so that the pressure increases from slightly above that of one atmosphere to forty atmospheres, it is said that there is no increase of a vapor pressure out of proportion to rise in temperature; that is, as the temperature has increased there is simply a corresponding increase in pressure. If, however, kerosene is treated in the same manner, the pressure rises in proportion to the rise in temperature until a temperature of nearly 300° C. (572° F.) is reached, after which there is an increase in pressure entirely out of proportion to the increase in temperature. Similarly, when treating 26° Baumé petroleum residuum, there is a noticeable increase of pressure out of proportion to the increase of temperature when the latter

[1] U. S. Patent 534,295, Feb. 19, 1895.
[2] J. S. C. I. 1916, 1254; United States Patent 1,203,312, Oct. 31, 1916.

is between 300° C. (572° F.), and 325° C. (617° F.), that is, at those temperatures the pressure rises rapidly with slight increase in the temperature While these temperatures and pressures are only approximate and vary greatly according to the substance treated and the products desired, it is noticed that in each case there is a certain temperature below which the rise in pressure corresponds to the rise in temperature, and above which the rise in pressure is out of proportion to the rise in temperature. While the exact nature of the reaction is not understood, new products are produced rapidly above the " breaking point," but are not produced below this temperature, and in treating any particular substance, the operator, by the proper observations of temperature and pressure determines what the breaking point is.

From this point the temperature is raised very slowly, since in making gasoline from kerosene it is found that a sweeter product is
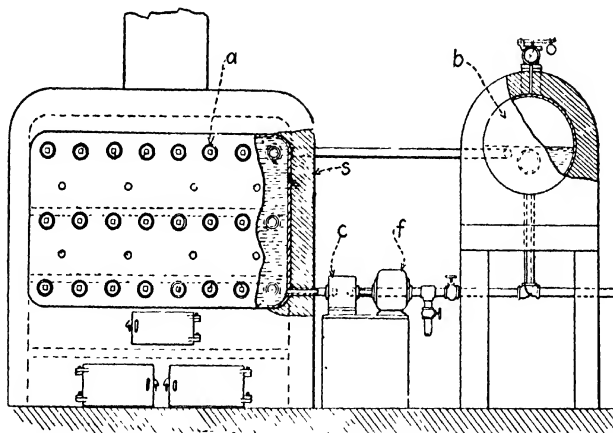
Fig. 111. — Pressure still in series with pipe still, according to W. M. Cross.

derived when the increase in temperature above the breaking point is very slow. The process is continued until there is no longer any rise in pressure out of proportion to the rise in temperature. The contents of the converter are then allowed to cool without releasing the pressure except such a decrease as results from the cooling. The product of the converter is then drawn off into the reheater and the temperature in the reheater maintained at a point which will vaporize the product desired. By varying the temperature in the reheater different products can be condensed and separated.

Seigle [1] forces petroleum oils in spiral streams through the spaces between horizontal, concentric, cylindrical metallic shells. He uses

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[1] United States Patent 567,751, Sept. 15, 1896.

an apparatus part of which is shown in Fig. 112. The openings at the ends of each pair of concentric shells are closed by means of flanges, as shown at C. Such a pair of shells constitutes a unit. The several units are connected together
by means of expansion bends. Baffles cause liquid which is passing through the spaces between the concentric shells to traverse a spiral path. The liquid enters at A and leaves at B. Heat is supplied by hot combustion gases which travel in the direction indicated by the arrows.
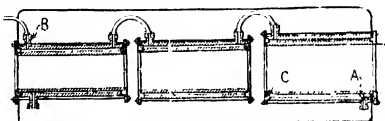
Fig. 112. — Device proposed by Seigle.

Parker [1] describes a method the purpose of which is to avoid the production of carbon as much as possible. It is based upon the belief that at 1000° F. (538° C.) the higher boiling hydrocarbons are more stable as regards ultimate decomposition, i.e., decomposition yielding free carbon, than are the lower boiling oils. Fig. 113 shows how this purpose is effected. The crude oil undergoes three treatments in the cracking chambers. First it passes through coil A, which is one inch in diameter and fifty feet in length. Here the oil is heated to 400°–450° F. (227°–232° C.) and attains a pressure of 100 pounds per square inch. The oil then passes through a nozzle or injector, then into and through a steam-jacketed pipe B. The effect of the nozzle gives the oil and oil vapors an increased velocity. The pipe B is heated to 800°–900° F. (427°–182° C.) by means of superheated steam generated in superheater E. Prior to the entrance of the oil from the coil A to the jacketed pipe B about 10 per cent of superheated steam is injected into the oil.

After leaving the jacketed heater B the oil is passed through an expansion drum C provided with a spiral or helix to give the oil a whirling, centrifugal and progressive movement. In other words, the oil, which is really in the form of a vapor, is forced to circulate or rotate very rapidly, and as it is traveling at the rate of approximately 100 feet per second, the heavier parts of the vapor are, it is stated, forced outwardly from the center of the conveyor and exposed to the hottest temperature within the retort (about 1000° F. (538° C.)). The gas or lighter parts of the vapor are said to stay nearer the center of the screw or helix, and consequently a more uniform breaking of the oil as it passes through the expansion drum will result, avoiding the superheating of gaseous products. From the expansion drum C oil passes to a pressure drum where carbon is allowed to settle before the oil continues

[1] J. S. C. I. 1917, 704; U. S. Patent, 1,226,990, May 22, 1917.

to a cooler, in which the temperature is reduced to approximately 300° F. (149° C.).

Noad[1] uses horizontal N-shaped retorts. Fig. 114 delineates a horizontal sectional and a vertical elevational view, respectively, of a
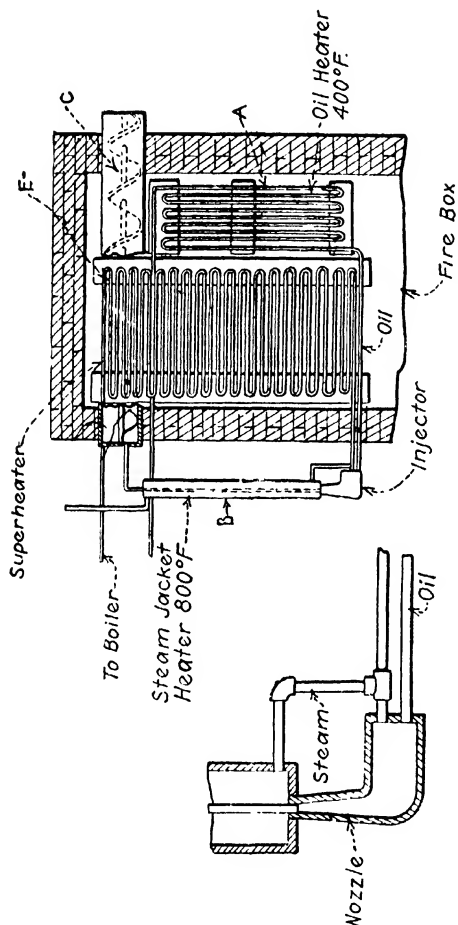
Fig. 113. — Method advocated by W. M. Parker.

single retort setting. Water and heavy oil, for example, American solar oil of 0.863 specific gravity, are simultaneously dropped into these retorts. The retort is packed with scrap iron. The mixed vapors of oil and steam are subjected to a cracking temperature (in the case of

[1] U. S. Patent, 971,468, Sept. 20, 1910.

the above-mentioned oil about 900° F. (482° C.)) in contact with the iron at about atmospheric pressure and are then led away to stills, where the light oils are distilled off.   The residue from this distillation
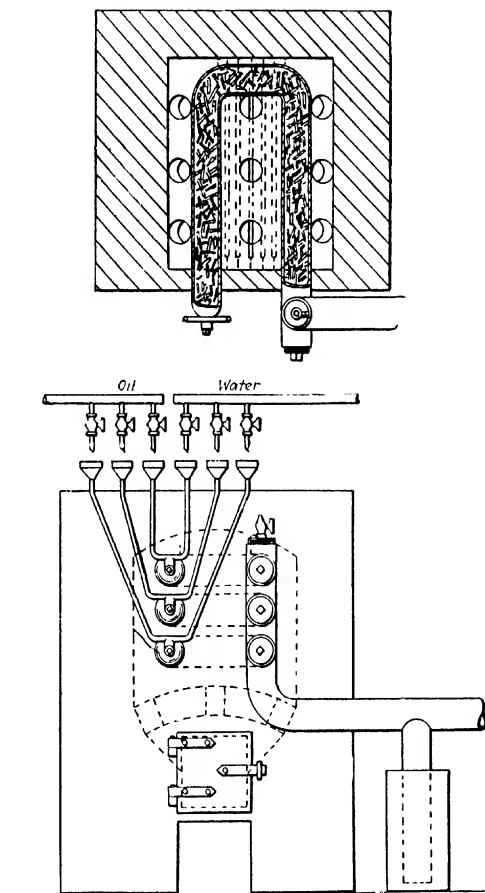
Fig. 114. — Noad's retorts.

is'returned to the retorts.   One of the main features of Noad's process is the injection, into the retorts, of water in a liquid state, together with oil, in a liquid state, into the heated chambers.

Lewes and Redwood [1] are of the opinion that the latent heat of the

[1] Report of Lewes, V. B., and Redwood, Boverton, concerning Noad's process, London, E. C., March 2, 1910.

oil and liquid water greatly assist in keeping the temperature well
below 500°C. (932°F.). Concerning Noad's method, **Lomax** [1] says that

"in 1908 **Noad** and **Townsend** [2] proposed to decompose oil and water in liquid form
in the presence of each other and of highly heated iron in the form of scrap or
the like, claim being made that the iron acted as catalytic agent. This patent was
taken over by the New Oil Refining Process, and was followed by several others
under these names in 1911 and following years, [3] in which claims were made for
other packings in the retorts, and for temperatures of 1000°–1200° F. (538°–649° C.).
In the process as worked, the retorts were horizontal iron tubes about 12 ft. long
and 9 in. in diameter, and 9 tubes were built in one battery. These retorts were
packed with iron turnings rolled into the form of cartridges, fitting loosely into the
tubes to facilitate removal. The retorts were heated by oil or gas burners, the gas
for the latter being produced in the process, and the temperature, about 600° C.,
was kept under recorded pyrometric control. The oil and water were fed into the
retorts by separate pipes in the proportion of about four parts of oil to one part
of water. On dropping into the retorts vaporization instantly occurred, and the
vapors thus formed were quickly removed from the sphere of action by means of
an exhauster, passing first through a dephlegmator where the heavier products
were condensed, and then to a water-cooled condenser, where the main fraction of
the cracked oil was collected. The gas, still charged with light spirit, was passed
through scrubbers to recover these bodies, and finally into a gas holder for use
as fuel in the plant. The condensed cracked oil and spirit-laden scrubber oil
were passed through topping stills to remove all spirit, and were then mixed with
the heavy condensates from the first dephlegmator to be returned through the
retorts. Solar oil was the crude material used in the plant, and also as scrubber
oil, the quantity used in the scrubbers each day being so arranged that it was
equivalent to the quantity required in the converters next day. The spirit from
the topping still was refined with sulphuric acid and alkali, and then steam-
distilled through dephlegmators, giving a water white motor spirit, a solvent or
paint spirit with flash point over 73° F. and a residue suitable for varnish, rubber
substitute, etc. The yields of finished products obtained from the original solar
oil employed were: -- Motor spirit, 40 per cent: paint or solvent spirit, 13 per
cent: varnish substitute, 13 per cent: gas, 30 per cent: carbon and loss, 4 per
cent. In this process the spirit produced had the inherent defects, and also the
good qualities, of cracked spirits, but difficulties were encountered in the working
on a large scale, and after some months of operation the process was finally
abandoned."

Carbides of iron, copper or aluminum, bauxite, broken bricks, coke,
charcoal, aluminum oxide are some of the refractory materials men-
tioned by 'the **New Oil Refining Process** (Co.) and **Neilson** [4] as contact

[1] The Pyrogenesis of Hydrocarbons, J. Inst. of Petroleum Technologists,
1916 (3).

[2] Noad and Townsend, British Patent 13,675 (1908).

[3] (a) New Oil Refining Process and Neilson, British Patents 28,460 (1911);
20,074 and 20,075 (1912); (b) New Oil Refining Process and Rossini, British
Patent 13,726 (1913); (c) Noad, British Patent 3607, Feb. 13, 1912.

[4] British Patent 28,460 (1911).
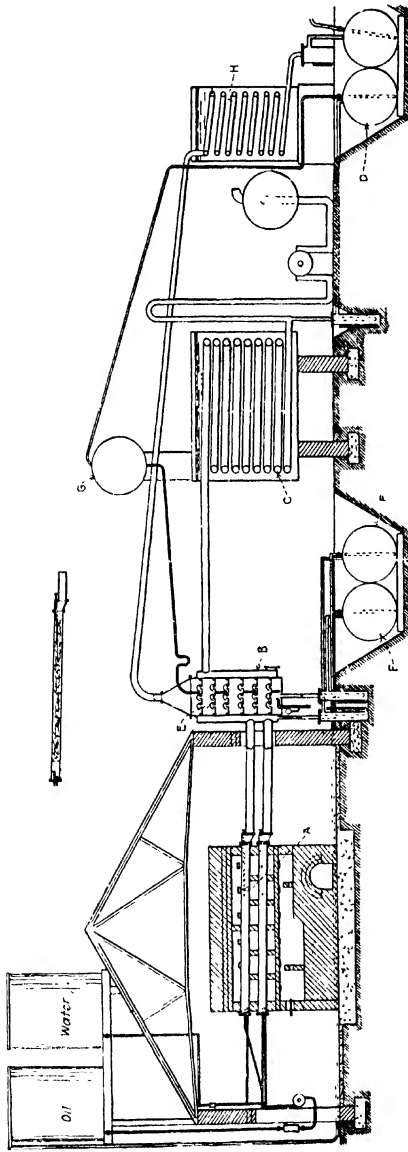
Fig. 115. — Type of apparatus employed by New Oil Refining Process and Neilson

bodies.   These when heated to 1000°–1200° F. (538°–649° C.) are said
to assist in producing naphtha from heavier oils, in the presence of
steam.   The contact bodies are placed in a tube or retort made of
refractory material, while water, as such, and oil, in the liquid form, are
introduced.   The use of water in the liquid state and oil in the liquid
state and the contact bodies mentioned above are said to yield a large
amount of light naphtha and very little carbon and gas.   In previous
work [1] scrap iron was the contact material mentioned.[2]   In both proc-
esses air is excluded from the retort.   Apparently the vapor formed
by passage of the oil and water through the retort is merely removed
at about atmospheric pressure and condensed.
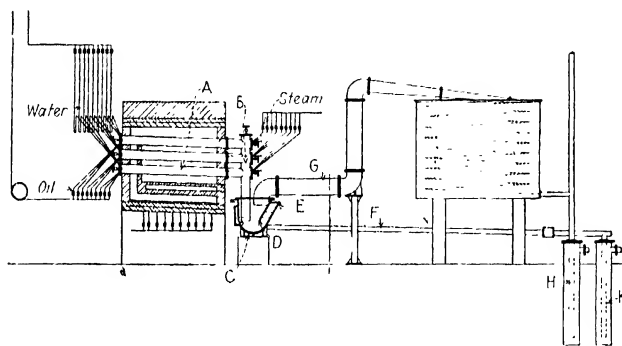
Fig. 116. — Apparatus of the New Oil Refinery Process and Neilson

Not long afterward this concern disclosed several types of improved apparatus.
Crude oil was the material cracked.   One such apparatus is shown in Fig 115.
Oil and water are separately pumped into a battery of six slightly inclined hori-
zontal retorts and are here subjected to cracking temperatures.   (A, Fig 115.)
The gaseous products then pass through the apparatus B, which is a combined
dephlegmator or separator and " re-run " still, that is, the inner shell E, the " re-
run " still, containing the partitions, is entirely separate from the outer shell B,
or dephlegmator.   Heavy products which condense in the shell B run through a
trap into the adjacent storage tank from which they are pumped back to the
charging tank.   Non-condensed material passes on through the condenser C into
a storage tank D.   Distillate collecting in D is pumped to an overhead reservoir
G from which it flows back into the " re-run " still E.   Residues from this distilla-
tion flow into the tank F and are, in turn, pumped back into the charging tank.
The light distillate from the " re-run " still is condensed in the condenser H.

In another method proposed by the **New Oil Refining Process** (Co.)
and **Neilson** [3] the retorts are in a vertical position.   Oil and water are

[1] British Patent 13,675, June 27, 1908.
[2] See Noad's Process.
[3] British Patent 20,075, Sept. 3, 1912.

separately fed into each retort, heavy material drawn off at the bottom and lighter oils passed up to a reflux condenser. This reflux condenser returns unconverted oils to the retort. The removal of heavy material at the bottom is said to prevent pitching and coking.

In 1913 [1] a further improvement in apparatus is noted by the same company. This is characterized by a design (Fig. 116) which allows the retorts to be readily cleaned without closing down the fires. There are three sets of retorts, each set consisting of three retorts, one above the other and connected to a vertical header, *B*. Each header dips into a "safety box" *C*, and from the top of this safety box a vapor pipe *G* leads to a condenser. When it is desired to clean the retorts, the oil and water feed is shut off and steam is blown through the retorts and header to expel vapors. Water is then introduced into the safety box until the outlet of the header *B* is sealed. This shuts off communication with the condenser and drain pipe *F*. The removable ends of the retorts can now be detached and the retorts thoroughly cleaned. At the same time, the manhole *E* can be opened for cleaning the "safety box." When operation is resumed the water is removed from the safety box.

The retort, as in all the other methods described by the New Process Company, are packed with pieces of iron, or refractory material. The methods are based on the use of working pressures about atmospheric.

Lomax [2] states that in the New Oil Refining Process particular attention was paid to the question of cleaning the tubes, which were arranged in such a way that a whole battery of 9 tubes could be cleaned while hot, the entire operation from shutting off of oil and water to starting again taking about 20 minutes.

Lamplough [3] describes a process for converting heavy hydrocarbons into motor spirit, which consists in forcing a mixture of water or steam and heavy oil, in constant proportions (about 10 per cent of water) under pressure through a tubular cracking device (shown in Fig. 117) which is heated by means of fuel oil. The tubes contain nickel rods. The re-

Fig. 117. — Lamplough's tubular cracking apparatus, employing steam in the presence of nickel.

action mixture in contact with the nickel is subjected to a controlled cracking temperature and superatmospheric pressure. The pressure used may be considerable, as, it is stated, pressure tends to reduce the amount of any volatile spirit carried away by the permanent

[1] British Patent 13,726, June 12, 1913.

[2] In the Pyrogenesis of Hydrocarbons by **Lomax, Dunstan** and **Thole**, Journ Institution of Petroleum Technologists, 1916 [3].

[3] J. S. C. I. 1913, 743; British Patents 19,702, Aug. 28, 1912 and 28,101, Dec. 5, 1912.

gas. In one phase of the process the pressure is regulated by a relief valve on a receiver at the end of the condenser coils (not shown). Interconnected pumps, communicating with separate vessels containing water, heavy hydrocarbon oil to be converted, and fuel oil for heating the tubes execute the functions of delivering the oil and water in a definitely and constantly maintained ratio to the cracking tubes, and at the same time automatically proportion the temperature of the cracking chamber to the rate of oil-and-water passage through the cracking tubes by regulating the fuel oil supply to the burners. It is stated that to obtain the maximum yield of spirit, it is desirable first to pass the mixture of heavy oil and water or steam rapidly through the retort at an incipient red heat so as to avoid as far as possible the production of fixed gas, and after distilling off the light spirit, to repeat the operation with the remaining undistilled oil several times, with the retort at successively higher temperatures.[1]

T. E. Yaley[2] maintains a retort (having a conical bottom) at a cracking temperature and intermittently causes small quantities of oil to flow into the retort near the top or apex of the conical bottom, with a result that the oil is spread over the lower conical surface of the retort and rapidly vaporizes. This produces a pressure which temporarily prevents flow of oil into the retort.

Vapors are led through a run-back and are condensed under atmospheric or slightly sub-atmospheric pressure. The process is characterized, partly, by intermittent flow of oil to the cracking retort.

Dubbs Process [3]

The design and operation of the Dubbs plant is given in the report of a committee of the Western Refiners' Association to its members. Extracts from this report are quoted as follows:[4] "The plant proper consists of a cracking coil made up of ten lengths of 4-in. extra heavy lap-welded pipe, each 20 ft. in length, jointed on the ends by return bends. This coil of 4-in. pipe is placed horizontally in a furnace in two rows, six of the pipes being in the lower row and four in the upper row. The furnace temperature is maintained at approximately 1540° F. The outlet of the 4-in. coil is connected to an expansion chamber which consists of four 20-ft. lengths of 10-in. common extra heavy pipe. These pipes are connected in series by means of return bends so as to form an ex-

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[1] See also U. S. Patent 1,229,098, June 5, 1917.
[2] U. S. Patent 1,329,450, Feb. 3, 1920.
[3] See also Dubbs, J. A., Chap. 4, p. 10.
[4] By F. W. Padgett, Chem. Age (N. Y.) July, 1920, p. 229.

pansion chamber approximately 80 ft. long. These 10-in. pipes are positioned horizontally in a chamber and are not heated, but insulated on the outside to prevent loss of heat by radiation.

" The raw oil is fed into one end of the 4-in. coil by means of a force pump, and as the oil passes through it is heated to about 820° F. and is then discharged from the other end into the 10-in. expansion pipes, which are maintained approximately half full of oil. The vapors are liberated from the oil and pass up through connecting goose necks to a manifold; then to vapor lines leading to a spiral vapor condenser, and finally into a water-cooled condenser. A pressure of about 135 lb. per sq. in. is maintained on the entire apparatus. The unvaporized portion of the oil in the 10-in. coil is continuously drawn off from the end of the last unit."

In regard to the Dubbs process, it should be noted that the cracking takes place in a two-phase system. The following summary gives the results of a test run of 168 hours' duration:

Total gas oil treated	20,952 gal.
Total uncondensable gas	25,851 cu. ft.
Fuel used — equivalent of 3677 gal. of 14 Bé. fuel oil	
Products (per cent yield of original oil charged):	
Gasoline (440 end point) (58.59 Bé.) .	26.29 per cent.
Kerosene (40–41 Bé.)	14.11 per cent.
Pressure distillate bottoms (31–32 Bé.)	27.19 per cent.
Residuum (13–14 Bé.).	24.71 per cent.
Loss................................	7.70 per cent.
	100.00

CHAPTER XIII

TUBE AND RETORT CRACKING IN THE VAPOR PHASE

The Use of Catalytic or Contact Bodies

Meldrum [1] passed heavy oils and solid paraffin of low melting point through an iron pipe heated to a visible red heat. The tube was filled with broken stone or spent shale. He obtained illuminating and lubricating oils.

Sabatier [2] decomposes heavy oils by leading their vapors over catalytic metals, which are prepared, for example, by reducing the corresponding oxides with a reducing gas at an elevated temperature. [3]

The unsaturated light hydrocarbons resulting from the decomposing treatment are then mixed with hydrogen and again passed over catalytic metals, to effect a hydrogenation, or saturation.

The process consists of two parts:

1. In subjecting the vapors of crude petroleum or petroleum already deprived of its naphtha content, to contact with finely divided metals heated to temperatures ranging between 400° C. (752° F.) and dark red heat. There is a partial decomposition of the vapors into gaseous products, consisting of a mixture of hydrogen, hydrocarbons and liquid products, a considerable proportion of which distills below 150° C. (302° F.). The residue boiling above 150° C. is mixed with fresh oil and again put through the process.

The metals which may be used are: — pyrophoric iron, powdered copper, silver, iron, nickel, or cobalt made by reducing the oxides with hydrogen or other reducing gas, powdered zinc, finely divided platinum. Mixtures of these metals are also used, obtained by mixing the metals or by reducing the mixed oxides or by chemical precipitation. The metals may also be supported on inert material. The carbon deposit which settles on the catalyzers diminishes their activity and must be periodically removed. In the case of zinc this may be done by the action of steam at 500° C., in which case carbon dioxide and

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[1] British Patent 376, August 6, 1869.

[2] French Patent 400,141, May 21, 1908.

[3] See also Sabatier and Mailhe, U. S. Patent, 1,124,333, Jan. 12, 1915; also Haller, Sabatier and Senderens, French Patent 376,496, filed June 14, 1906, Published Aug. 10, 1907.

hydrogen are formed. Or the carbon may be removed by burning it with air or oxygen. In this case the metallic oxide simultaneously formed must be again reduced by hydrogen or a reducing gas.

2. The liquids formed as above indicated are largely composed of oxidizable, unsaturated hydrocarbons, which possess a disagreeable odor. To convert the evil smelling products into more desirable ones, it is necessary to hydrogenate the cracked products by mixing them with hydrogen and passing at 150°–300° C. (302°–572° F.) over finely divided metals.

Nickel reduced from the oxide by means of hydrogen is most suitable, although it is possible to use cobalt, copper, iron or platinum.
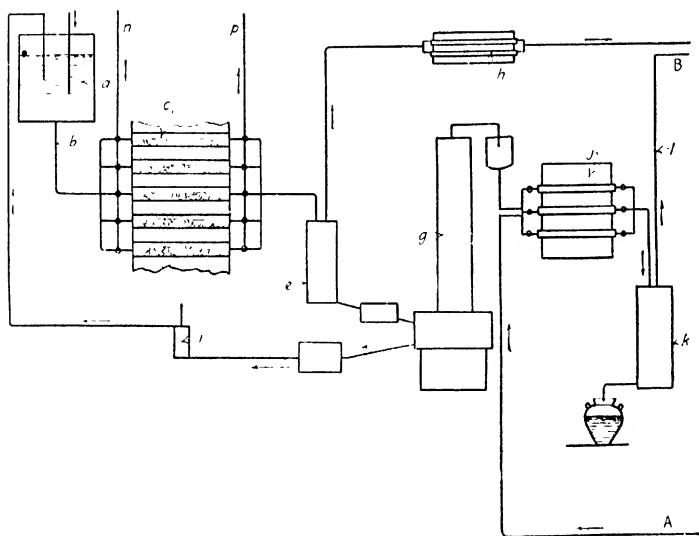
Fig. 118. — Sabatier's method of cracking and hydrogenating the light oils

The gases from the cracking operation may be used in several directions:

1 As fuel for heating the cracking chambers, and redistilling the products of the cracking operation.

2. They may be compressed and shipped in cylinders for commercial consumption, as illuminating gas, in a manner similar to the employment of Pintsch or Blau Gas.

3 Passed over copper coated iron, heated to a red heat   It is stated they are decomposed in this way largely into carbon and hydrogen $C_nH_{2m} = {}_nC + {}_mH_2$.   In Fig. 118, h is the decarburizer to carry out this operation, the resulting hydrogen being used in the hydrogenation of the light oils

Figure 118 shows a diagram of a proposed commercial plant in which the cracking and hydrogenating operations are coordinated.

C represents a number of cracking chambers, connected in parallel. The chambers are provided with independently functioning valves and supply pipes so that any chamber or chambers can be independently operated, for example:

(a) Heated, for cracking purposes.

(b) Cooled, for repair or cleaning.

(c) Supplied with steam or air, as already described, through pipes *n* and *p*, in order to destroy carbon deposits.

a is the oil supply and *e* the condenser for cracked products. Gases which are not condensed in *e* pass through the decarburizer *h*, are decomposed into carbon and hydrogen and the latter is led into a gasometer at *B*. Material which is condensed in *e* flows into the fractionating still *g* where a separation into heavy and light oils takes place. The pump *i* conducts the heavier oils back into reservoir *a* while the light oils pass up through the fractionating still and after admixture with hydrogen from the gasometer *A*, pass into the hydrogenator *j*. *k* condenses the condensable products issuing from the hydrogenator while the excess of hydrogen and steam produced in *j* pass into the gasometer at *B*.

Gasometers at *A* and *B* operate alternately.

Sabatier found, however, that the catalytic activity of the finely divided metals mentioned above was destroyed by the deposition of carbon, and, to overcome the difficulties thus encountered, the metals are mixed with difficultly reducible oxides.[1]

The revised method consists in substituting, for the metals mentioned above, either the same metals, or the oxides or salts capable of producing them by reduction, mixed with neutral materials free from silica, such as magnesia, alumina or bauxite, lime, baryta, strontium or carbonates of the same oxides, graphite or any other neutral substance which does not contain considerable quantities of silica, or even the same metals, oxides or salts, either alone or mixed, "associated" with the neutral materials by an agglutinant which does not contain silica (glue, dextrin, starch, etc.). The agglomerates thus formed are molded in the shape of regular or irregular briquets, balls, tubes, coatings or fragments of any desired shape. These dry agglomerates, or the mixtures above referred to, are introduced into tubes of iron, cast iron, steel, etc , or into earthenware tubes, provided inside with a non-silicious coating, such as magnesia, baryta, bauxite, etc.

The first stage is carried out between 400° C. and bright red heat. When oxides are used in place of metals in the mixtures described, or in the agglomerates referred to above, the reduction of the oxides can be effected by means of vapors of hydrocarbons, at the same temperatures as that present at the beginning of the first stage. The first stage, in which vapors of burning oils or crude petroleums or petroleums deprived of naphtha, any residues of petroleums, shale oils or resin oils, are passed over the above mentioned catalytic mixtures, results in producing gases and volatile liquids easy to condense, and in the formation of carbon deposits on the mixtures or agglomerates, which, after a long time, reduce their activity. When the reduction of activity has become considerable, it is not difficult to revivify the catalyzer, first by the action of steam at the same temperatures, the steam being substituted for the vapors of hydrocarbons This action changes the metal into oxide, the gas generated during the reaction consisting of a mixture of hydrogen, carbon oxide, and carbonic anhydrid.

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[1] Sabatier and Mailhe, U. S. Patent 1,152,765, Sept. 7, 1915.

The first stage of the process includes therefore two steps; during the first of which hydrocarbons are introduced, which initially reduce the oxides formed to metal, and subsequently are partly transformed into gas, liquids more vola-
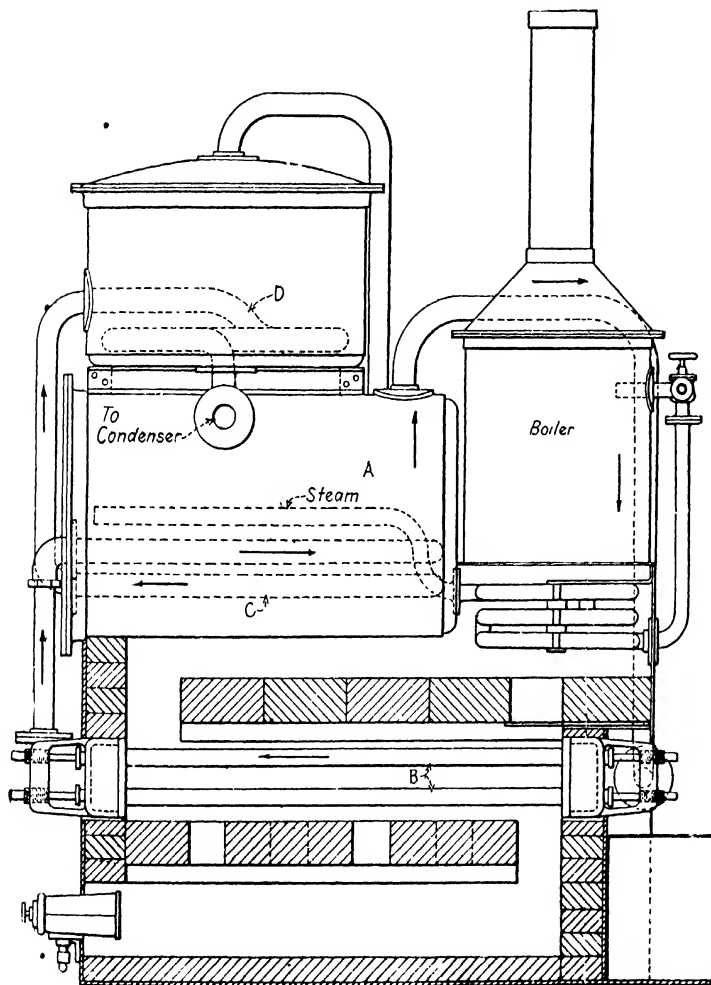
Fig. 119. — Method of Valpy and Lucas.

tile than the original product, and carbon, under the action of the divided metal thus produced; and the second step, in which steam is used to remove the carbon deposited in the mass during the first step. These two consecutive steps can be repeated indefinitely.

The volatile portions distilling below 150° C. (302° F.), obtained during this first stage, may be separated out and converted into saturated non-oxidizable hydrocarbons, by hydrogenation. The liquid portions obtained, which are not volatile below 150° C. (302° F.), are repeatedly treated like the original hydrocarbons, until the conversion is completed.

Examples of catalytic mixtures: (1) Mix thoroughly 40 parts by weight of calcined magnesia with 100 parts of porphyrized iron filings.

(2) Mix thoroughly 50 parts of calcined magnesia and 120 parts of iron filings. Add a solution of dextrin, so as to obtain a paste which is molded to form briquets, and dried.

(3) Sixty parts of bauxite and 100 parts of porphyrized iron.

(4) As perfect a mixture as possible of 20 parts of calcined magnesia, bauxite (60 parts) and oxide of iron (150 parts) is reduced to paste by means of glue. From the paste are formed briquets, which are dried in a slow heat.

(5) Thirty parts of precipitated alumina and 80 parts of porphyrized iron are mixed. The whole is agglutinated with a solution of dextrin, and the mass used for making briquets.

See also Sabatier and Mailhe, Chem. Abs. 1916, 273; British Patent 16,791, July 14, 1914.

Valpy and **Lucas**[1] vaporize heavy oil in a still (A, Fig. 119) by means of superheated steam (3 to 8 per cent steam, to the oil, both measured as liquids) and pass the mixed vapors through heated nickel tubes (B, Fig. 119). The hot reaction products expand and then pass through tubes located in the still, then through tubes in the supply tank (D), thus preheating the charging stock, and finally through a dephlegmator (not shown). The tubes may be packed with nickel catalyzer in addition to being constructed of nickel. Hydrocarbon gases may be used in place of steam.[2]

Ellis and **Wells**[3] describe the results of experiments with several forms of tubular cracking apparatus.[4] Using kerosene of 42 Bé. (specific gravity 0.814), yields of gasoline (boiling point up to 150° C.) of 18–20 per cent were obtained at 450°–600° C. (842°–1112° F.). By distilling off the gasoline, retreating the residue, and scrubbing the gaseous reaction products with oil, yields of 40–45 per cent of gasoline were obtained. The gasoline was denser than normal gasoline of the same boiling point, had a higher refractive index, and was unsaturated; the iodine value of the distillation fractions was higher the lower the boiling point, a fraction of boiling point below 70° C. (158° F.) for

[1] British Patent 20,470, Sept. 10, 1913.

[2] For methods of preparing metal-containing contact or catalytic bodies see O. D. Lucas, U. S. Patent 1,168,404, Jan. 18, 1916.

See also Valpy and Lucas, J. S. C. I. 1915, 707, 71; British Patents 2838, Feb. 3, 1914; 12,653 May 22, 1914; 18,923 Aug 21, 1914.

[3] J. Ind. Eng. Chem., 1915, 1029–1033.

[4] See also Ellis, U. S. Patent 1,341,975 June 1, 1920.

example, having an iodine value of 310, whereas the fraction boiling at 150° to 160° C. had an iodine number of about 50. On standing for a long time the gasoline became darker in color, and when subsequently distilled, a violent reaction occurred at about 160° C. (320° F.), resulting in the production of a dark brown viscous oil. A similar reaction occurred at about 110° C. (230° F.) on distilling under diminished pressure (6–10 mm.). The viscous polymerized product reacted violently with sulphur and with sulphur chlorides, a viscous oily mass being produced. Hydrogenation improved the odor of the gasoline, changed the color from light straw color to water white, and destroyed the tendency to polymerize. About 16 to 18 per cent of condensable gases was produced during cracking. The gas contained up to nearly 40 per cent of olefins and small quantities of carbon dioxide and monoxide, oxygen and hydrogen. When it was treated with chlorine, a liquid of specific gravity 1.176 and boiling point 90°–200° C. (194°–392° F.) was formed. No difference could be detected between the effects of using water and of steam in the cracking process. The yield of gasoline diminished when the ratio of water to oil was greater than 30:70. The gasoline left a gummy residue when used in a carburetor, but gave satisfactory results after hydrogenation.

Ellis[1] cracks kerosene and obtains gasoline, by subjecting the kerosene to successively increasing degrees of heat. Instead of immediately cooling the resulting products, they are then given an opportunity to become more stable by being subjected to successively decreasing temperatures before passing to a condenser. In this way, gummy dienes and trienes, di- and triolefins, are rearranged into more stable products and the resulting gasoline is improved.

The apparatus used is shown in Fig. 120. In the furnace setting are arranged a series of nearly horizontal pipes *A* which have a slight inclination so as to zigzag across the chamber from top to bottom. *B* is an inlet pipe for kerosene Through this pipe also may be fed water or aqueous solution (a diluted solution of ammonium nitrate may be used). The pipe *B* communicates with the uppermost pipe of the series *A*. The lowermost pipe of the series *A* has an outlet *C* controlled by a valve. The pipes are connected by means of the headers *D* in which are placed plugs which enable the tubes to be opened and viewed from end to end, or readily cleaned. The second series of tubes is indicated by *E*. These tubes form a rising system leading from the lowermost tube of series *A* and are connected one with another in a manner similar to the series *A*. The series *E* is given a greater inclination than the series *A* and the uppermost tube of the series *E* is below the uppermost tube or tubes of series *A*. The uppermost tube of series *E* communicates with a riser *F* connected with an air condenser, one member of which yields its condensation products to the pipe *H* which passes through a

[1] J. S. C. I. 1918, 49A; U. S. Patent 1,249,278, December 4, 1917.

condenser trough filled with water and connects with a trap which is fitted with the draw-off K. The riser M provided with a valve allows the separation of gas and uncondensable products. From the trap a pipe equipped with a valve leads to the uppermost pipe of the tubular heating series A. A pump may be inter-
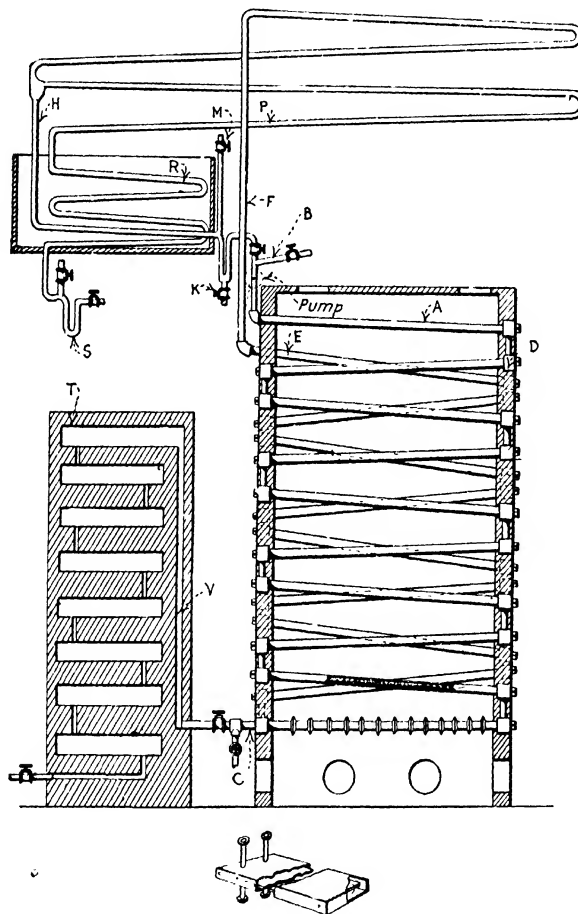
Fig. 120 — Ellis' proposal for obtaining stable cracked naphtha.

posed in this pipe to facilitate the removal of the liquid products from the pipe H and trap, especially when the tubular system is operating under pressure. A second wing or member of the air condenser P serves for the condensation of lighter products, more particularly the naphtha which passes through the condensing pipe R to the trap S.

The function of the rising tubular series E is mainly that of digestion and final reaction which ordinarily does not require an extremely elevated temperature, but is a time reaction involving rearrangement of molecules to establish equilibrium. The term "equilibrium" has reference to the molecular condition of the components of the gasoline, resulting from the reactions during the digestion of the products of the heat decomposition of the material treated, in which reactions unsaturated or otherwise unstable bodies produced, act by chemical union with the gases produced by the decomposition or by union with each other or by polymerization, to produce stable compounds. This digestive function, as it may perhaps be termed, may obtain in the apparatus T, and the tubular heating series E dispensed with, this being done in the apparatus shown, by inserting the plug in the lower end of the lower member of the series E so far as to prevent the flow of vapors through E. An extension of the pipe C enters the apparatus T and connects with the riser V which in turn communicates with the digestion chambers. These digestion chambers are of considerable length and width, but relatively small height, and connected one with another by means of pipes. The digestion chambers are embedded in heat insulation material so that radiation loss is reduced

The tubes of series A are filled with catalytic material which also may be the case with the rising series E, although the uppermost of these are sometimes left open but the lower of these tubes carry catalytic material. In order to secure a greater heat conductivity, especially when the pipes or tubes are large, nickel, iron or steel balls, disks or irregular shaped metal fragments are used throughout the tubular system, thus affording a more rapid decomposition and transfer of heat and some or all of the pipes may be equipped with fins as shown in the lowermost tube of the heating series A.

The tubular rising series E in contrast with the descending series A extends from the zone of high temperature into one of relatively low temperature so that while the flow of the material along the series A is into zones of higher and higher temperature that of the material in the series E is into zones of lower and lower temperature, and thus as the series A is functioning as a decomposition system, the rising series E serves more as a digesting and equilibrium-effecting system, an effect which may be secured to a greater or less degree, according to circumstances, by the digesting boxes in the apparatus T. The decomposition of petroleum oil normally gives rise to unsaturated products and the naphtha resulting from treatment of this character is unstable By allowing the constituents of the materials formed by reaction to digest in the space afforded a satisfactory quality of naphtha is said to be obtained.

The production of gasoline from kerosene or for that matter from crude oil and various distillates involves a splitting up of heavy molecules into molecules of lower molecular weight often with the simultaneous generation of hydrogen and other gases and the production of carbon, soot and tar. It is important to minimize the production of coke, soot and tar as these block the heating pipes more or less and when a catalyzer is used are liable to coat its surface and impair its efficiency. The hydrogen which is set free by the decomposition should be given an opportunity to recombine which is entirely possible in view of the fact that unsaturated bodies are produced during the splitting operation

Conditions are adjusted to provide a temperature for the escaping gases leaving the heating chamber that shall range between 150° C and 250° C. (302° F. and 482° F.). In the lower portion of the heating apparatus a temperature several hundred degrees higher, between 400° C. and 600° C. (752° F. and 1112° F.), de-

pending on the oil employed, is desired. For kerosene boiling from about 150° C. (302° F.) upward, a temperature of about 500° C. (932° F.) in the lower sections is recommended. Fractions which require high temperatures to decompose are superheated to 600° or 800° C. (1112°–1472° F.) in the lower heating tubes and then pass upward through risers E into zones of progressively decreasing temperature while equilibrium is being established, or into digesting chambers T for the same purpose.

Diolefin formation appears to be a side reaction which takes place to a fairly considerable extent in the cracking of oils. The diolefins are, however, rather unstable, reactive hydrocarbons and appear as intermediate products in many high temperature cracking processes. Frequently diolefins are found in some types of cracked gasolines and a discussion of the conditions favoring the formation of these interesting hydrocarbons is appropriate.

Although their presence in cracked gasoline for motor fuel is very undesirable they are nevertheless of commercial value in the preparation of useful products of polymerization and their preparation is made the subject of a study by **G. Mersereau.**[1] The conditions which he defines for a maximum yield of diolefins are interesting since they point out how diolefins are formed and we may therefore deduce how to avoid these conditions in avoiding the production of diolefins in a cracked gasoline.

The raw materials used are the same as those used for making gasoline, namely, heavy crudes, gas oils, still residues, etc. It is said that diolefins are more easily formed from straight chain paraffin or olefin hydrocarbons than from cyclic or aromatic oils. This would naturally be expected. In the production of diolefins, high pressures are avoided. It might, merely from this, be concluded that a certain amount of pressure is desirable in making good gasoline. It is also specified that at a certain point in the decomposition the vapors should be suddenly cooled so as to prevent destruction of the diolefins and thereby obtain a maximum yield; for instance that high heat damages the gas carrying the diolefins. Temperatures around 700° C. (1292° F.) with 800° C. (1472° F.) as a maximum and 600° C. (1112° F.) as a minimum are best. The time factor is an important one since *the diolefins are apparently formed by secondary reactions at the expense of the gases directly formed from the oil; and these secondary reactions require an appreciable time.* Their velocity appears to follow however a descending curve. As a rule, the heating should be continued, it is stated, until the per cent of diolefin in the gases ceases to increase rapidly and then the gases should be at once

[1] U. S. Patent 1,282,906, Oct. 29, 1918.

cooled to arrest further internal reactions. In passing the vapors and gases through a narrow hot tube, with about 2 seconds exposure to heat, a gas containing 4 to 5 per cent of diolefins is said to be obtained, while by heating for 5 seconds, somewhat in excess of 8 per cent can be secured. As high as 11 per cent with 30 seconds exposure has been found; but ordinarily, and particularly where the gas is to be used again to make more diolefins, it is better to cease heating when the diolefins are around 8 per cent.

Gradual cooling under pressure would therefore appear to be conducive to a minimum yield of diolefins. Contact bodies and catalysts in the decomposing tubes appear to be avoided in securing a maximum amount of diolefins. The reaction chambers, moreover, are specified to be tubes of small diameter ($\frac{1}{2}''$-$\frac{3}{4}''$) and short length (10''-50'').
• Coky carbon appears to decrease the yield of diolefins.[1]

It is stated also that a good conversion to form olefinic gases can be attained with no more than 6 inches of travel (narrow tubes $\frac{1}{2}''$-1'' internal diameter) through a heated zone, while 90 inches and more of travel are not injurious under proper heating conditions. With a shorter length of travel, up to say 30 to 45 inches, the proportion of diolefins is about 4 to 5 per cent of the total gas and the ethylene is present in much larger amount than propylene and the butylenes. With a longer travel of the oil vapors through a heated zone, up to say 90 inches, the proportion of propylene relative to ethylene rises and the percentage of diolefins also increases up to about 8 per cent.

This proportion of about 8 per cent represents, it is stated, a maximum limit; a limiting "partial pressure." This formation of diolefins appears to be at the expense of the olefins proper. If the heating be interrupted when this maximum is reached, the gas cooled to remove oil vapors and the diolefins removed and recovered, upon reheating the gas to about the temperature at which it was originally formed, a fresh yield of diolefins is said to be formed. Here again the maximum limit seems to be about 8 per cent. On removing the newly produced diolefins and once more heating the residual gas, more are produced, the limit again seeming to be about 8 per cent. Repetition of the treatment will give a fourth yield; but this time the amount is generally only about 6 per cent. Subsequent treatments ordinarily are stated to be hardly worth while.

Ellis[2] finds that the decomposition of oils heavier than gasoline, like kerosene, gives rise to products which often form a smoke or fog in the gases which are evolved, this fog passing through the water condenser even when the water-cooling medium is chilled with ice, and sometimes even after passing through scrubbing towers containing oil which ordinarily would be expected to remove suspended particles.

To avoid this loss he passes kerosene through heated conduits to raise the temperature of the vapors to 550°-600° C. (1022°-1112° F.)

[1] Mersereau, U. S. Patent 1,308,802, July 8, 1919.
[2] J. S. C. I. 1917, 447; U. S. Patent 1,216,971, Feb. 20, 1917.

and contacts these vapors with catalytic material in the presence of water vapor. The vapors containing the products of dissociation are removed, passed through the usual air and water condensers where the gasoline is largely separated from the heavier oil and the gases containing the resistant mist-forming particles are conveyed to a compressor by means of which the gases are brought to a pressure of 300 pounds per square inch. The gases are further chilled and the light liquid products separated under these circumstances are collected and added to the light products derived by ordinary condensation. The gases which are freed from the condensable products are carried to the heat decomposing portion of the apparatus and mixed with the vapors of the raw material. Approximately the same volume of gas is added to the raw material as would be produced by the decomposition of the raw material without the added gas so that in the case of kerosene vapors producing about 10 per cent of gaseous bodies about 10 per cent of recovered gas would be charged or a sufficient amount mixed with the oil in advance of heating to aid in the reduction of the gross amount of gas generated during the operation.

The apparatus is operated under pressure, by allowing the gas compressed during the operation, after removing the mist-forming particles, to enter the heat decomposing apparatus in such a way that the pressure of these gases is utilized to maintain the heat decomposing zone under several atmospheres.

J. S. Lang [1] describes a " pipe " still for decomposing heavy oils to obtain volatile hydrocarbons. It consists of a system of preheating tubes located in the flue of the furnace setting, within which is situated the decomposing or superheating coils. A reflux condenser is connected with the exit from the superheating coils. Condensates heavier than those it is desired to obtain as ultimate products are collected at various points in the condenser and returned to the superheating coils. The heaviest condensates are returned to the cracking coils at the hottest point of the latter and condensates of lesser specific gravity at successively cooler points. In other words the heaviest condensates have to pass through the entire cracking zone while the lighter condensates pass through successively decreasing areas exposed to cracking conditions.

By the method of **Cassal** and **Gerrans** [2] petroleum is converted into benzene and toluene, by passage in a finely divided form without added water or air through heated graphite or alumina, and collecting the resulting gaseous products. For example, burning oil is admitted in a

[1] U. S. Patent 954,575, Apr. 12, 1910.
[2] Chem. Abs. 1918, 2126; British Patent 117,087, June 29, 1916.

stream into a retort containing graphite heated to 700° C. (1292° F.). The oil vaporizes upon contact with the retort and passes through the graphite in the form of vapor.   The alumina and graphite may be used together or in succession.

Wells [1] makes gasoline from kerosene in the vapor state in contact with a nickel catalyzer which consists of a packing of jack stones coated with nickel and contained in annular jackets concentrically surrounding a central flue.   This flue is a combustion chamber and is packed with refractory material.   It is heated by a mixture of gas and air.

It is stated that the crude gasoline obtained by this operation without hydrogen is rather dark in color and has a slightly unpleasant odor in addition to containing bodies which polymerize with great ease and which are therefore undesirable.   The gasoline is therefore passed with hydrogen over nickel.

• Robertson, Nelson and **Petrol Patents, Ltd.,** [2] convert high-boiling hydrocarbon oils and residues into low-boiling hydrocarbons by bringing them in the liquid state into contact with pumice stone or sandstone heated to 500°- 800° C. (932°-1472° F.) in a closed retort, and condensing the resulting vapors.   These are removed by a pump and are fractionally condensed under pressure, e.g., 16 atmospheres.   Viscous hydrocarbons, such as tars, are preheated to increase their fluidity.   In treating tar for the production of toluene, a temperature of 750° C. (1382° F.) is employed.   Liquid fuel of the nature of gasoline is produced from " fuel oil " at about 550° C. (1022° F.).

Testelin and **Renard** [3] crack petroleum oils in a horizontal retort which is connected with superimposed preheating tubes made up into a grid.   In Fig. 121 is shown part of the apparatus.   The pipe S supplies oil under about five atmospheres pressure through the injector G to the preheater F.   The injecting action is brought about by means of steam which is also applied through the injector G.   The mixture of oil and steam preheated to about 400°–450° C. (752°–812° F.) in F passes through retort J where cracking takes place, assisted by catalytic material contained in the retort.   The products of the reaction leave the retort J through pipe K and pass into a condensing apparatus (not shown).   The exit pipe K is provided with a pressure reducing valve H' and an air or " cushioning " chamber H, which acts as a shock absorber.

The heating elements are small, operate under a high pressure (about five atmospheres) and at high temperatures (as high as three or four times the mean of

[1] U. S. Patent 1,248,225, November 27, 1917.
    See also **Wells**, U. S. Patent 1,232,454, July 3, 1917.
[2] Chem. Abs. 1919, 1636; British Patent 10,981, July 29, 1915.
[3] British Patent 16,881, Aug. 11, 1908; U. S. Patent 1,138,260, May 4, 1915.

the boiling of the liquids) and the highest temperature retort contains a porous, refractory, catalytic mass; the petroleum is atomized under pressure and brought into the heating elements by steam; and intense heat is directly applied during a very short traverse; the particles are practically instantaneously volatilized and broken up into new compounds and the entire heat treatment of each particle is completed in a very brief period, in one operation, without intermediate condensations and revaporizations.

From the heating elements the product is discharged, suitably reduced in pressure, to fractionating condensers, which separate the several permanent compounds. The oils of commerce, whose density or specific gravity varies from 0.800 to 0.820, treated in this apparatus, undergo modifications more or less pro-
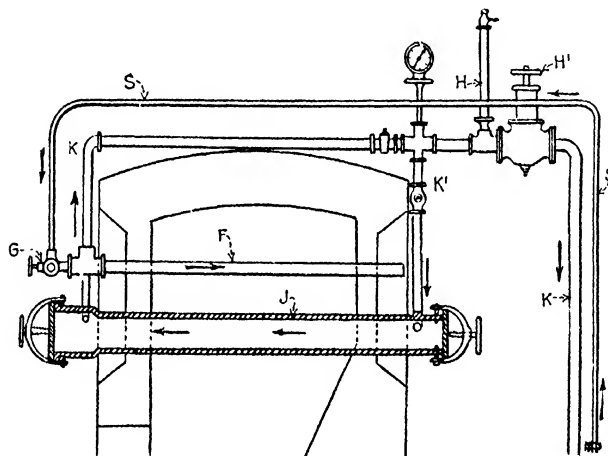
Fig. 121. — Apparatus proposed by Testelin and Renard.

found, and controllable by varying the pressure, the temperature and the duration of the treatment. The product includes distillates, isomeric transformations, and products of decomposition. The liquid is changed in density. Light and heavy hydrocarbons are formed simultaneously, the proportions of the several kinds depending upon the pressure, the temperatures and the duration of the treatment of a given quantity. The heavy products can be re-treated and transformed into light spirit.

The greatest proportion of light and highly volatile product is obtained by superheating until there is a slight production of permanent gases. The condensing apparatus (not shown) consists of reflux, fractionating condensers and a final condenser. The primary heater or volatilizer F is protected from the fire by a diaphragm and is heated by convection. The cast iron retort extends through the combustion chamber and contains a catalytic obstruction made from suitable refractory material, such as clay. Its protruding ends are closed by yoke-mounted, screw-closed caps. The oil supply system (not shown) includes a closed regulating pressure-tank into which oil is pumped by a force pump. The operation of the apparatus is as follows: — The furnace E is lighted and steam at about five at-

mospheres is admitted through the steam pipe to the primary heater F, and thence to the condensers. The primary heater F is maintained at a temperature not less than 400° or more than 450° C. (752°–842° F.), and the retort J at a red heat. This is facilitated by the location of the retort in the combustion chamber exposed to the direct heat of the fire and the separation, by a diaphragm, of the retort from the primary heater. As soon as the primary heater F is heated to the desired temperature, the pump is started to supply oil, and the steam valve and the injector G are adjusted so that the oil and water issuing from the condensers are substantially equal in volume.

The oil is atomized by the steam and with the latter is carried in a finely divided state into the primary heater F, where both are superheated and converted into vapors, and then into the retort J and through the catalytic obstruction. The products then pass to the pressure regulator H', which reduces the pressure suitably for the condensing plant. If the temperatures tend to become too high, more oil and steam are admitted, the rates of work and abstraction of heat are increased and the temperatures tend to become normal; while if the temperatures tend to become too low, less oil and steam are employed, rates of work and abstraction of heat are decreased and the temperatures tend to rise. However, proper maintenance and regulation of the furnace fire in great measure obviate the necessity for varying the rates of oil and steam supply. Because of the intimate contacts of the superheated oil and steam in the retort J and catalytic obstruction, the reactions generally occur, it is said, practically in detonations, which cause rapidly succeeding pressure oscillations or shocks. These are cushioned and rendered harmless by the shock absorber or air chamber H. The proper reading of the gage is the mean of such pressure oscillations.

The distillates and heavy hydrocarbons from the reflux and other stills can be returned to the heating elements for additional treatment and suitable arrangements can be made for that purpose, so as to produce the maximum proportion of spirit. If the reactions occur at too low a temperature, little or no light spirit will be produced; while if the temperature be too high too much gas and too little spirit will be produced.

The operation is analogous to that of the fixing chamber of water gas plants, in which the enriching oil practically at atmospheric pressure is subjected to a very high temperature and thereby converted into permanent gas. In this apparatus the temperature is lower because the desired product is "spirit," not gas, and the pressure is very much higher because the desired reactions are functions of both temperature and pressure and as the pressure is increased the reaction-temperature necessary to produce spirit becomes lower. Therefore by maintaining a high pressure it is practicable to cause the desired reactions by a temperature that will assure the production of the maximum proportion of the desired spirit, with the minimum of gas and heavy hydrocarbons.

Methods that Avoid the Use of Catalytic Packings

Von Groeling[1] distills and cracks hydrocarbons by passing the vapors from a still through externally heated cracking tubes in which they are mixed with liquid hydrocarbons. The vapors are thus scrubbed, and the liquid hydrocarbons are preheated and fed to the still. The

[1] Chem. Abs. 1914, 3501; British Patent 10,213, April 30, 1913.

distillation is effected by superheated steam and by means of a furnace,
the gases from which afterwards pass over the cracking tubes.   The
cracked vapors are separated in a dephlegmator into fractions.   In
some cases the cracking tubes are fitted with removable worms.   The
temperature in the still and cracking tubes ranges from 350° to 500° C.
(662°-932° F.) and the operation is effected under a slight pressure.

Eldred and **Mersereau** [1] depolymerize heavy oils or residua, to form
unsaturated gaseous hydrocarbons of the aliphatic series; e.g., ethylene
and propylene, subjecting the oil in a vaporized state for a brief period
of time to a low gasifying temperature, by transmitting a current of
vapors past or over heated surfaces, the time of exposure of the oil to
the temperature used being insufficient to produce complete decompo-
sition.   The heated vapors and gases are removed from the zone of
heat, and quickly cooled to remove unchanged oil and the gases are
then treated to recover the unsaturated gaseous hydrocarbon.

Ethylene, propylene, the butylenes and the other gaseous compounds of this
aliphatic group, being of comparatively high reactivity, are of potential value as
raw materials for the manufacture of many chemical substances.   Ethylene, for
example, is valuable as a raw material for the manufacture of alcohol, ether,
aldehyde, glycol, ethylene chlohydrin, ethylene esters and vinyl derivatives.
Propylene and the butylenes are also materials which can be used in produc-
ing valuable substances.   Other unsaturated aliphatic hydrocarbons are possible
sources of synthetic caoutchouc.

It is asserted by Eldred and Mersereau that by heating oils which,
like many crude petroleums and residua, consist largely of carbon com-
pounds containing from 10 to 20 or more carbons in the molecule,
with a suitable control of the conditions, a depolymerization of com-
paratively simple and regulable type and without complex side reactions
can be produced.   Under proper conditions, it is said, the oil is broken
down mainly into gaseous compounds, having two carbon atoms, with-
out deposition of carbon or formation of tar.

The oils best adapted are crude petroleums composed of oils boiling at tempera-
tures from 150° C. (302° F.) to 200° C. (392° F.) or above 200° C. (392° F.) (that
is, containing hydrocarbons with more than 10 carbons) or petroleum residua from
the manufacture of gasoline and kerosene.   Low boiling oils composed of hydro-
carbons with 6 to 8 carbons in the molecule are less well suited.   On exposing
such high boiling hydrocarbons in vapor form to temperatures around 700° C.
(1292° F.) and within 50 to 75° C. on either side of that point, a regularly gasify-
ing depolymerization sets in with the production of low molecular gaseous hydro-
carbons without any great amount of other synthetical or analytical side reactions
as long as vapor of unchanged oil still remains in the sphere of action.   Such

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[1] J. S. C. I. 1917, 999A;   U. S. Patent 1,234,886, July 31, 1917.

[2] See also preceding description of the Mercereau process, page 280.

vapor seems to have, it is stated, a shielding action on the products. With the disappearance of unchanged oil, decomposition of the products begins. Coky carbon should be absent since in its presence, probably because of a special catalytic power, the regularity of action would disappear.

To obtain the desired regularity of operation, the time of exposure to the heat should be comparatively short, not over a few seconds, there should be sufficient contact of the vapors with the heated solid materials conveying the heat, and the operation should be so conducted as to preserve at all times an excess of heavy oil vapors in the sphere of reaction, or, in other words, the reaction should not be pushed to a finish as regards the particular body of oil vapors under treatment. And this excess should be well distributed throughout the body of gas and vapors; there should be no stratification of the comparatively light gases free of the relatively heavy oil vapors. In the presence of this excess of oil vapor, the reactions go forward much more smoothly while the excess is not lost since it can be condensed out of the reaction products and then returned in admixture with the fresh oil to the reaction zone. With proper regulation of conditions no important amount of carbon will be set free; and such as may occur will be soft and in the nature of lampblack. If hard, coky carbon be once deposited in the reaction chamber by undue heating or otherwise it exercises, as stated, a detrimental catalytic effect, causing far-going cracking with formation of more hard carbon. Its presence should therefore be guarded against. The heating is done in a narrow externally heated tube, which is of steel, iron, copper or clay. Ordinary heavy walled steel or cast iron piping is suitable. It is heated by gas, fire or electrical heating, as long as the heating is uniform and controllable. It is best not much over 1.5 inch internal diameter and may be only an inch or 0.5 inch. Other forms of containers than cylindrical tubes may be used but it is desirable not to have any portion of the heating chamber more than an inch away from the wall. This is for a number of reasons. One is that capacity of a chamber increases faster than the area of the walls; and the larger a chamber the more heat units must be sent through a square inch of wall per second to maintain a given temperature throughout that chamber; i.e., the hotter must be the walls. The figure given represents a convenient limit. While it is desired to heat the oil vapor and gas uniformly to some temperature around 700° C. (1292° F.) a temperature of 800° C. (1472° F.) represents a danger limit which should not be exceeded. At 800° C. (1472° F.) breaking down of ethylene, propylene, etc., is apt to begin. Another reason for the limit given is that with chambers of large section

it is difficult to prevent stratification — a separation of oil vapors and gas. And a stratum of gas, free of oil vapors, is apt to suffer damage at temperatures which would otherwise be safe.

It is thus best to operate with narrow tubes. The length of these may vary somewhat; but for the production of ethylene they are best comparatively short; the heated length is from 6 to 30 inches. The linear area of the tube exposed to heating should be comparatively short; or in other words, merely enough to bring the vapors to the desired temperature without prolonging the heating action. Six to 10 inches of heated area with a tube of small diameter are sufficient; though the tube advantageously may be several times as long. With a half-inch iron tube, in producing ethylenic cracking, the tube may be so heated over about 6 inches of its length as to make it a just visible red and may have 18 to 30 inches of length beyond the heated area so arranged as to give a tolerably uniform temperature drop through that length down to about 150° C. Should coky carbon form within the tube the operation should be at once interrupted until it is removed, since the tube will soon plug up and the quality of the gas will suffer at once. The tubes are horizontally arranged as this facilitates quick travel of unstratified homogeneous currents of mixed vapor and gas therethrough.

It is best to supply the oil to the tube as liquid, flooding the feed end of the tube and allowing vaporization to take place inside rather than supply it as preformed vapor or as spray since this procedure has been observed to afford more uniform action. The amount of feed should be so correlated to the size and the heated length of the tube and the temperature that a substantial amount of easily condensable heavy oil vapors will emerge with the effluent gaseous products of reaction. This amount with advantage is not less than 10 per cent of the amount of oil fed in, and may be more, up to 35 to 50 per cent. With 10 per cent, in normal operation it may be said that often from a quarter to a half are cracked, oily products and the residue is unchanged original oil. In normal operations, the recovered oil is free of tar.

This excess of oil is readily recovered by air-cooling the gas exit conduit and is returned to be mixed with fresh oil for re-passage. The excess of oil serves several important purposes. It acts to shield the unsaturated gases from breaking down, as a diluent to reduce the partial pressure of ethylene, propylene and other bodies, and in its condensation to scrub the issuing gas, removing vapors of easily volatile oils which may be formed. Gas formed in a given tube at a given temperature, freed of the excess of oil and run back through the same tube at the same temperature (but in the absence of oil vapors) is apt to be modified considerably.

The particular temperature to be used may vary somewhat; but should be around 700° C. (1292° F.) in making ethylene as a principal product, not varying more than 50 to 75° C. either way. About 800° C. (1472° F.) is, as stated, a danger limit. Operating with a ¼-inch tube having a heated length of about 30 inches, with an internal temperature of about 650° C. (1202° F.) the formation of gases is slow, though such gas as is formed is of good quality for the present purposes. With this heated length of tube at this temperature a considerable amount of cracked, low-boiling liquid bodies will be formed; and proportionately low gas. At 660° C. (1220° F) to 700° C. (1292° F.) with such a tube, the conversion is good; at 750° C. (1382° F.) it is quite rapid and care must be taken to insure quick passage of gas with short exposure to heat.

With a half-inch tube heated for 30 inches and with enough oil feed to give 10 to 50 per cent condensable oil in the effluent product, the gas emerging will be white and foggy (from condensing oil). Any tinge of brown shows formation of tar and irregular operation. On air-cooling the effluent product, as by passing it through 8 or 9 feet of similar tubing, heavy oil will be condensed out and may be removed, carrying with it any gasoline-like hydrocarbons or other low-boiling liquid hydrocarbons. The gas will contain 45 to 50 per cent olefins (mainly ethylene with a varying proportion of propylene and butylene), 4 to 5 per cent apparently other aliphatic unsaturated hydrocarbons and the residue mainly ethane with a little hydrogen. With a heated length of 90 inches in a quarter inch tube and an oil feed rapid enough to give substantial amounts of unchanged oil emerging, the proportion of propylene and butylene will be raised and that of ethylene lowered while the amount of the other unsaturated aliphatics will increase materially. With a tube of this length, the time of exposure of the oil to the heat will be about 5 seconds in normal operation.

The mixture of oil vapors and gases emerging should be cooled to condense out the heavy oil, and with it such light oils as may be present. Air cooling or water cooling may be employed; the latter particularly with comparatively low temperature operation (say around 650° C (1202° F)) where a considerable proportion of " cracked " gasoline may be formed. It may next be led through a filter to remove foggy particles of entrained oil.

After removing the heavy oil by cooling, the gas is purified   If made from oils containing aromatic constituents it may contain some benzene, toluene, etc , and in this case it is scrubbed with wash oil to absorb and remove them. The condensing oil in cooling will take out some benzene; but as this oil is returned for re-passage the quantity of benzene increases until it appears in the gas. From the wash oil, benzene and toluene may be recovered by simple distillation. With crude oils consisting of aliphatic hydrocarbons, aromatic hydrocarbons are not formed to any extent, it is said.

The composition of the products will vary somewhat with that of the original oil and with the details of operation. However, presuming a good petroleum with the vapors exposed to a temperature of about 660° C. (1220° F.) to 700° C. (1292° F.) for, say 2 seconds, as in running through a half-inch steel pipe heated for about 6 to 30 inches with 10 to 40 per cent oil passing on beyond for condensation, the gas will usually run about 45 to 55 per cent olefins; 4 or 5 per cent acetylenic gases; 4 or 5 per cent apparently other unsaturated aliphatics; a little hydrogen and methane and the residue mainly ethane. Of the olefins, two-thirds or more, it is said, will be ethylene with the residue mainly propylene and a little butylene. If the time of exposure to heat be increased, as by running the oil through 80 to 90 inches of heated quarter inch tubing the other aliphatics may go up to 8 or 9 per cent and the proportion of propylene will increase.

The olefins and other unsaturated aliphatics may be absorbed and removed, allowing the ethane, methane and hydrogen to go forward to serve for combustion purposes. Or the products may be chlorinated. For example, the gas may be

treated with chlorine or bleaching powder, etc., to produce condensable halides of
the various olefins and diolefins, and these condensed or absorbed out to leave
the ethane. With plenty of chlorine, the ethane may also be chlorinated, par-
ticularly in the presence of actinic light. Admixing the gas with air or oxygen
and passing over catalyzers such as platinum or palladium, various useful oxi-
dized products may be obtained and condensed or absorbed, leaving the ethane.

The apparatus used is shown in Fig. 122.

A is a bank of short narrow tubes mounted in parallel and heated by a
burner. These tubes are about 30 inches long by an inch to 1.5 inches internal
diameter and are made of heavy steel. At one end, the tube receives heavy oil
from a main and at the other it is connected with an air-cooled conduit. This
conduit is six to eight feet long. As shown, the tube is provided with caps at
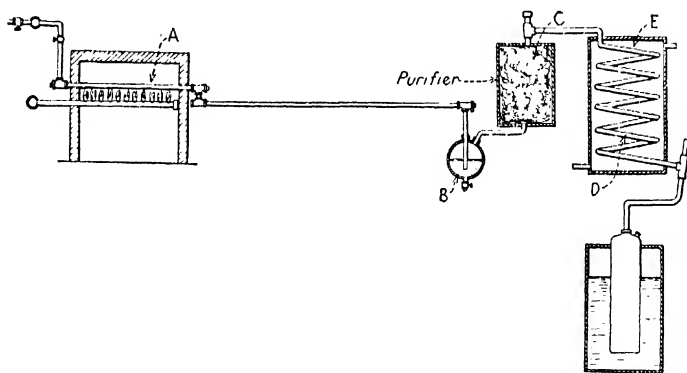
Fig. 122. — Apparatus for manufacture of olefins and diolefins, proposed
by Eldred and Mersereau.

each end by the removal of which it can be readily cleaned Cleaning is neces-
sary since if coky carbon is once formed not only is the gas injured but the narrow
tube usually promptly plugs up by the accumulation of carbon The presence of
a little carbon in the condition of lampblack or soot does no harm, this carbon
not having the detrimental catalytic effect of coky carbon. The air-cooled conduit
communicates with an oil main B where the oil, condensed in air cooling, accumu-
lates. It is removed from time to time and returned to the oil feeding device.
Beyond the oil main is a scrubber, for removing any entrained oil. As shown,
there is a purifier C containing excelsior or other fibrous material. Unless the oil
contains sulphur, this simple device is all that is necessary. Gas leaves the puri-
fier through a conduit. If it be desirable, as it generally is, to chill it further to
recover diolefins, the gas passes through coil D in vessel E kept filled with chilled
oil, calcium chloride solution or other liquid capable of withstanding temperatures
as low as 0° C. Condensed thereby, these diolefins flow down into a receiver
which is shown in a cooling casing kept filled with chilled oil, etc., while the gas
flows to a place of use. This chilling is desirable since these unsaturated ali-
phatics are of commercial value and worth recovering. Unless the original oil
contained aromatic constituents, as is the case with some varieties of petroleum,
the gas will not contain benzene, toluene, etc. If however aromatic constituents

exist in the original oil there will be some benzene and toluene in the gas, and these if not otherwise removed are condensed with the other chilled condensate from which they may be separated. It is preferred to use for the heating means a simple unobstructed cylindrical tube and to avoid the use of catalytic bodies, such as reduced nickel, copper, cobalt, etc., since any packing or other devices in the tube lead to delay in the flow of gas and, thereby, to damage in the ethylene. And in the presence of catalytic bodies, as noted with regard to coky carbon, the action is apt to be other than simple depolymerization.

The gas making operation is under ordinary atmospheric pressure. Small changes in pressure, either to less or to greater pressure, do not much change the results. Removal of the diolefins may be aided by the use of pressure or by the use of a little wash oil, from which they may be afterward distilled. If desired, the propylene and butylene may then be recovered as such by compressing the chilled gas to say 100 to 120 pounds pressure. This will leave the ethylene and ethane in gas form and condense out propylene and butylene as liquids. It is not ordinarily worth while to condense the ethylene and ethane by great cold and high pressure and then fractionate since the ethylene is so easily absorbed and removed chemically or physically. By condensing out the propylene and butylene, practically only ethylene is left admixed with the ethane and this mixture is proposed for making pure ethylene products. Similarly, the propylene and butylene (which can be easily separated by fractionation) can be so used   In most reactions however the various olefins give products which can be easily separated from each other and it is simpler to treat the mixed gases rather than to separate them

Where concentrated olefinic gas is desired this can be attained by physical, as distinguished from chemical, absorption. Many oily bodies, such as oil of turpentine, petroleums of aromatic nature, tar oils, etc., have much more solvent power for olefins than for ethane; and by washing the gas with these oils, the olefins can be partly removed in solution, leaving the ethane to pass forward as gas   The charged oils can then be stripped of their olefins by heat or vacuum, or both. In the case of some crude oils containing "colloidal carbon" or asphaltic constituents, some little coky carbon may develop at the point where the oil is vaporized, with a direct flooding feed of oil to the tube-retorts, but this does no harm as long as it does not extend to the portion of the tube which is hotter; the gasifying zone proper. A flooding feed keeps the portion of tube containing liquid oil at a temperature about the boiling point of such oil. Even at this, comparatively, low temperature an amount of, say, 2 per cent "colloidal carbon" in the oil is stated to develop 6 to 8 per cent coky carbon, apparently by catalytic action. With oils of this character and with a flooding feed, the heating should be managed so as to maintain the vaporizing zone distinct from the gasifying zone proper. With carbon-containing or asphalt-containing oils it is often useful to have a separate vaporizing device, giving a vapor feed in lieu of an oil feed to the gasifying tube-retorts.

In recovering the olefins, instead of chilling the gas, it may be scrubbed with cold concentrated sulphuric acid which is claimed to have but little action upon the olefins proper. The acid solution upon dilution separates polymerized unsaturated aliphatic hydrocarbons. By chilling the gas to about −15° to 20° C and then scrubbing the chilled gas with chilled heavy oil, the latter seems to take up some divinyl which may thus be recovered in a tolerably pure state, other unsaturated aliphatics having been separated by the chilling.

Seeger [1] passes the hot exit gases from his tube cracking operation first into vapor collecting tanks, then through condensing coils and finally into a storage tank. Fresh oil is led to the cracking coils through coils located in the vapor cylinders so as to utilize the heat in the treated vapors to preheat the fresh oil. Steam is generated in " flash " boiler tubes by the waste heat from the cracking furnace, passes into a steam reservoir and is then mixed with the oil before its treatment. The fresh oil, besides abstracting waste heat from the hot cracked vapors, also passes through the steam reservoir and thereby receives an additional preheating.
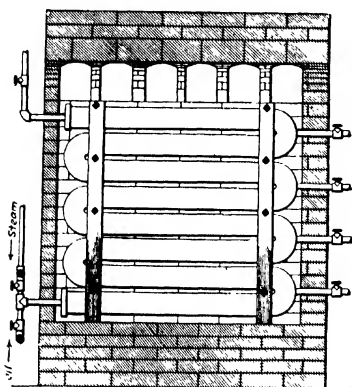
Fig. 123. — Seeger's pipe still for decomposing oil in the presence of steam.

The oil to be treated is pumped either through preheating coils in one or more vapor collecting tanks or through a preheating coil in the steam drum or through both. After being preheated the oil passes to each of the cracking coils, Fig. 123. The arrangement of the valve and connections is such that the steam and oil are supplied to the same portion of each cracking coil and that the supply of steam and oil to each cracking coil may be cut off or varied without disturbing the supply to the other cracking coils.

The cracking coils are subjected to a temperature not lower than 750° F. (399° C.) and the valves in the pipes leading to the storage tank are so set, and the supply of oil regulated so as to cause the maintenance of a high pressure in the cracking coils, for example, from five to twenty atmospheres. In order to minimize the production of free carbon, it is said to be desirable to introduce moist steam into the cracking coils, that is to say, steam whose temperature does not exceed 250° F. (121° C.). The pump, however, which furnishes water to the steam generators for producing this moist steam, also produces the pressure necessary to force it into the cracking coils. The temperature of the steam is regulated by regulating the degree of heat in the furnace chamber in which it is generated. Each of the cracking coils is connected to a vapor collecting tank and each of these tanks is connected to a condensing coil. The oil and water vapors produced in the cracking coils pass into the tanks, are condensed to a liquid state before issuing from the condensing coil and become separated in a settling

[1] J. S. C. I. 1918, 293A; U. S. Patent 1,259,786, March 19, 1918.

tank. Any uncondensed gas which reaches the settling tank is allowed
to escape from it through a gas relief valve.

Pielsticker [1] employs a coil in series with a still or horizontal cylin-
drical retort. The coil (D, Fig. 124) is made of iron pipes $1\frac{1}{2}$ inches
in diameter — the ends of which are open and the whole of the pipes
embedded or inserted into a solid block of iron or refractory material E,
provided with longitudinal channels through their entire length, into
which the pipes fit. The ends of the pipes are closed by means of an
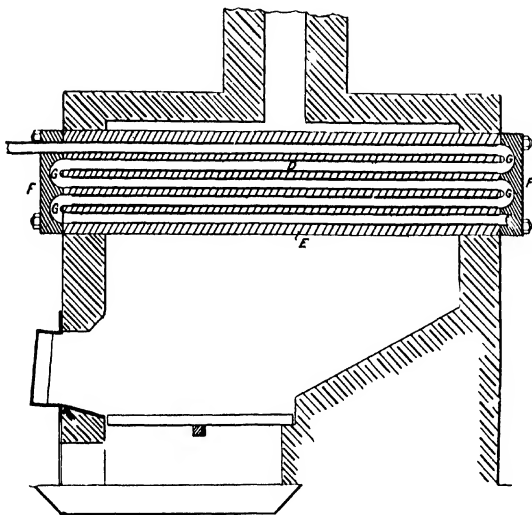
Fig. 124. — Cracking coil proposed by Pielsticker.

iron cover F, which is provided with channels G, so that the pipes D
form one continuous coil. In this case the cover F can be easily re-
moved and the pipes occasionally cleared of the carbon deposited inside
from the heated oil by simply forcing an iron rod through the length of
each pipe forming the coil. This construction of the heating-coil is said
to be a matter of great importance, since it is impossible to clear an
ordinary coil of the requisite length from any carbon adhering inside.
Moreover, the coil being loosely inserted into the block of iron or of
refractory material E, the whole length of the coil is permitted free
expansion, and the joints are consequently kept tight.

[1] British Patents 6466, April 28, 1890 and 1308, Jan. 4, 1891; U. S. Patent
477,153, June 14, 1892.

By passing the oil through the coil with great velocity the deposition of the carbon or heavy matter which would soon choke up the coil is prevented. This is done by graduating the diameter of the pipes D, forming the coil. For instance, the entire length of the coil is two hundred feet: the first fifty feet are constructed of two-inch pipes, the second fifty feet of one and a half inch pipes, and the last hundred feet of one inch pipes. Between the force pump and the inlet of the coil D a steam connection is provided for the purpose of emptying the oil contained in the coil D at the end of the operation by a steam blast into a retort into which the other end of the coil D leads; otherwise when the pumping is stopped the oil remaining in the coil D would speedily become carbonized and choke the coil.

The retort is provided with a number of vertical baffle plates causing the oil vapors to take a lengthened passage through the retort before they can enter the condenser. A passage is left in the lower part of the baffle plates in order to allow the flow of the tar or residuum to the draw-off cock.

When it is intended to produce lighter gravity oils, a valve is placed between the outlet of the retort and the condenser which may be kept open only so far as to create a certain pressure of the gases inside the retort.

If the manufacture of permanent gas or of very light oils is intended, the retort is directly connected with a second coil similar to the one described, steam previously superheated being simultaneously admitted with the oil vapors into the second coil by means of a steam injector provided for the purpose. The second coil may be kept under pressure by means of a valve and connected with an expansion-chamber or gas holder and condenser.

Swaton [1] carries out a cracking process in two steps by providing a distilling zone in which crude petroleum is distilled in a progressive manner, so that hydrocarbons of a lower boiling point are first distilled off, and, as the temperature is raised, hydrocarbons of higher point are distilled. The vapors distilled and consisting of progressively higher boiling products are passed through the cracking zone in which the temperature is maintained from 100° to 400° C. (212°–752° F.) higher than the boiling point of the vapors passing therethrough, adapting the cracking temperature to the particular hydrocarbon vapors passing to the cracking zone.

A (Fig. 125) indicates a still, B is a vapor conduit pipe leading to a reaction chamber C, which is a vertical pipe having an oval-shaped cross section in order to facilitate the heat transference from the surrounding furnace to reach the interior of the pipe. D is an expansion drum connected to the reaction chamber C from which a conduit leads to a dephlegmator E, provided with an outlet. The heavy hydrocarbons are led from the dephlegmator by means of a pump back to the still A. In operation the oil is distilled, the heat being raised gradually to about 400° C. (752° F.). The vapors of the hydrocarbons of pro-

[1] J. S. C. I. 1918, 294A; Chem. Abs. 1918, 1511; U. S. Patent 1,260,731, March 26, 1918.

gressively higher boiling points, as the heat is increased in the still, are
led to the cracking chamber C, where they are subjected to a temper-
ature of from 100° to 400° C. (212°–752° F.) higher than the temperature
of the entering vapors. The vapors coming from the still enter the
cracking zone at the top and pass downwardly. Since the process is
carried on at practically atmospheric pressure, this heating of the
vapors tends to cause them to rise and retard their downward passage,
prolonging the reaction time in the cracking zone. From the cracking
zone the vapors are led to the dephlegmator and condensers, which
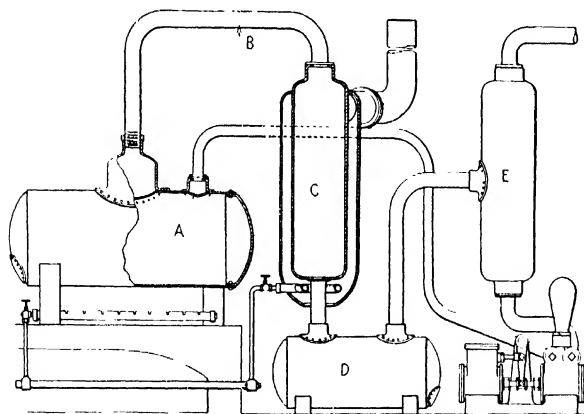
Fig. 125. — Still in series with vapor cracking chamber according to Swaton.

separate the heavy, the light hydrocarbons, and the incondensable
gases in the usual manner. The heavier hydrocarbons are led back
into the still to be subjected to the same cycle of operation. The
advantage is stated to consist in subjecting a current of hydrocarbon
vapors of progressively higher boiling points to a temperature of 100° to
400° C. (212°–752° F.) higher than the boiling point, thereby cracking
the hydrocarbons, avoiding excessively high temperatures, except at
the final stages of the cracking process, and producing a maximum
amount of gasoline, the yield being in some cases as high as 75 per
cent on the basis of oil used.

• **J. R. Miller** [1] cracks heavy distillates in a vertical retort or large
tube (Fig. 126) and then passes the products into a comparatively large
upright shell connected with the cracking tube. The pressure in the
shell is the same as in the cracking tube but the temperature is lower.
The upright shell is called a " synthesis tower." The purpose of the

[1] U. S. Patent 1,312,265, Aug. 5, 1919.

so-called " synthesis tower " is to obtain saturated low boiling products, that is to say, to cause the olefins and diolefins to become transformed into more stable bodies. This purpose, it is to be noted, is the motive underlying a number of other processes.

In the " synthesis tower " employed by Miller, there appears to be a stratification of vapors of varying density since very light gases are pumped from the top of the tower back into the cracking tube. From the " synthesis tower " " the vapors pass to a steam-heated receiving chamber," where a considerable back pressure is maintained, then to a
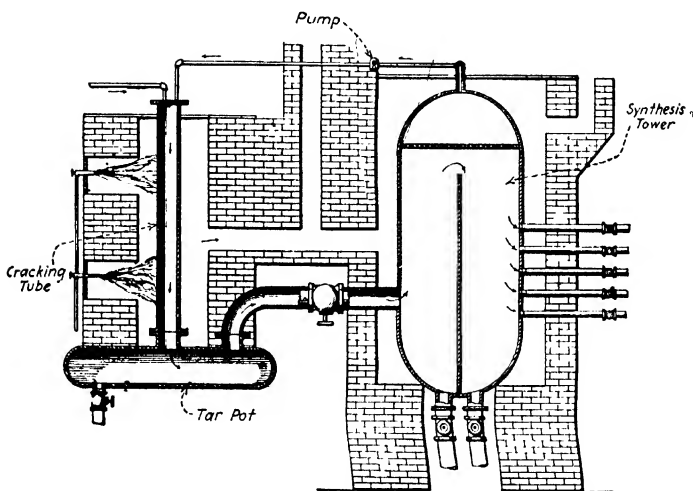
Fig. 126. — Miller's "synthesis tower."

separating chamber, also steam heated and finally to a cold water condenser. This process does not depend on condensation under pressure for its results.

Brownlee [1] defines the temperatures which are used in his tube cracking method as those in excess of the temperature necessary to vaporize all the vaporizable constituents of the oil being treated, if the oil were distilled at atmospheric pressure, disregarding residual tars and cokes. He subjects hydrocarbon oils to a counter current of gas, in a pipe system heated and maintained under pressure, in such a way that the heavier components separated at any point in the system undergo further treatment in the presence of a lesser concentration of the lighter vapors than at the point of separation.

[1] U. S. Patent 1,308,161, July 1, 1919.

The Synthetic Hydrocarbon Co.[1] use a vertical tube of refractory material heated electrically by a surrounding coil, provided at the top with a plug of loose refractory material through which liquid hydrocarbon is supplied to be gasified and then cracked. The products, which vary with the temperature, pressure, and the rate at which the gasified material flows through the heated zone, pass through a condenser to a liquid-collecting vessel having a pipe leading to a pump for withdrawing the gas at the top. Light hydrocarbon oils are produced at temperatures of 600°–900° C. (1112°–1652° F.) and pressures about 6 atmospheres. Permanent gases are produced in large proportion at a pressure of about 0.28 kilogram per square centimeter.
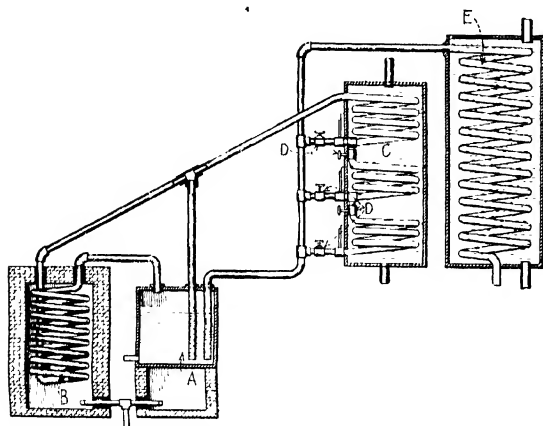
Fig. 127. — Still in series with cracking coil according to Wellman.

C. O. North [2] has made laboratory experiments on the cracking of heavy mineral naphtha, crude oil, and heavy kerosene to obtain a solvent gasoline, suitable as a rubber solvent. The oil was distilled under pressure from an iron still of about $1\frac{1}{2}$ gallons capacity and the vapor passed through a superheater consisting of a gas-heated tube connected with a reflux condenser fitted with a steam jacket. The heavier vapors were returned for further cracking while the lighter passed forward to be condensed and collected. Gases formed were collected in a small holder. The deposition of the carbon in the superheater it is said was not excessive at the temperature of working (a dull red heat). Heavy kerosene gave the most satisfactory results. The yield of the solvent gasoline (30°–130° C.) (86°–266° F.) was re-

[1] French Patent 480,653, Jan. 11, 1916.
[2] J. S. C. I. 1918, 3A; J. Ind. Eng. Chem. 1918, (9) 1038–1043.

ported to be up to 16.4 per cent and of motor gasoline (30°–150° C.) (86°–302° F.) up to 23 per cent.

The Ges. für Verwertung von Kohlenstoff Verbindungen [1] conducts hydrocarbon vapors, rising from a still, first through a vessel, the temperature of which is regulable and independent of the heating of the distillation vessel, and then to the condenser.

Wellmann [2] passes oil vapors from a still A (Fig. 127) through a superheating coil B and then into a reflux condenser C. The reflux
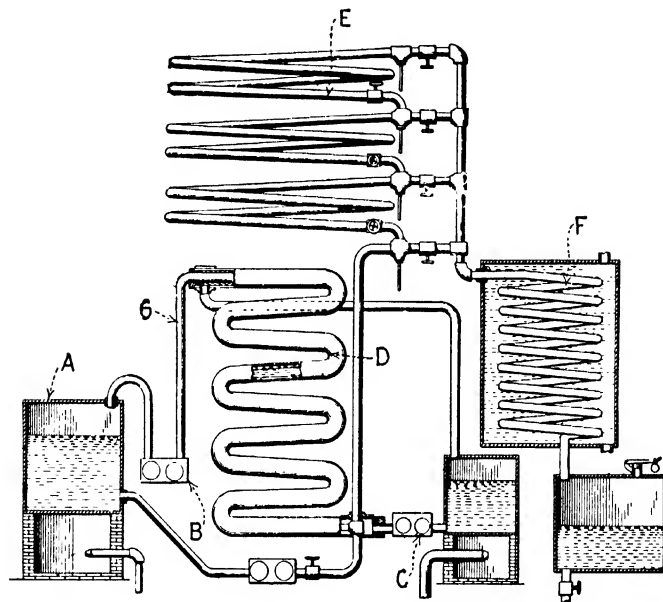
Fig. 128. — Wellman's apparatus for indirect heating of oil vapors.

condenser is composed of a number of independent units, connected in series. By suitably manipulating the valves D, any number of units may be employed, according to the gravity of the light oil which is desired and which receives its final cooling and condensation in the coil E. Cracking takes place in B at 750° to 850° F. (399°–454° C.) at atmospheric pressure. Condensation is likewise at atmospheric pressure. According to another process described by Wellman [3] hydrocarbon vapors are superheated under pressure in a pipe still, which is a double-walled affair, cracking taking place in the inner tube G, Fig. 128.

[1] Chem. Abs. 1916, 389; German Patent 284,118, July 20, 1912.

[2] J. S. C. I. 1918, 3A; U. S. Patent 1,245,291, Nov. 6, 1917.

[3] U. S. Patent 1,335,768, April 6, 1920.

Oil heated to a cracking temperature circulates between the inner tube
G and its jacket and supplies the heat necessary for cracking. Con-
densation takes place under pressure partly in the aerial condensers E
and partly in the water-cooled condenser F. A is a source of the
hydrocarbon oil to be cracked, and B is a force pump for applying
pressure to the vapors undergoing treatment. C is a pump for cir-
culating the heated oil which supplies heat to the cracking tubes.[1]
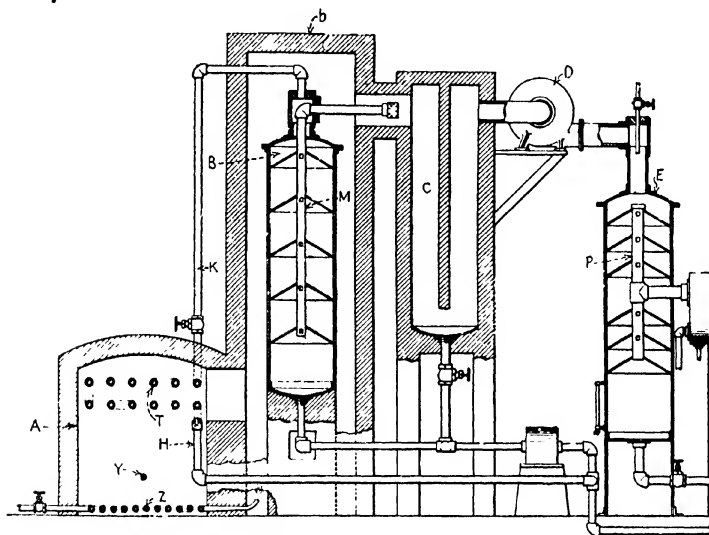
Fig. 129. — Method of Trumble.

In operating tube stills or retorts for cracking purposes Wellman [2]
considers it best to charge the tube still only to about one-tenth of its
volume capacity with the oil which is to be treated. Wellman claims
that by charging only to this amount a maximum yield of cracked ma-
terial is obtained. The operation is carried out intermittently, the tube
being charged with oil, heated under pressure and discharged. Tem-
peratures employed range between 750° and 900° F. (399° and 482° C.)
and the pressures vary between 100 and 600 lbs. The still is heated
until the pressure reaches the maximum point, when the contents of the
cracking tube are forcibly discharged and by such operation any carbon
which has formed in the tube is swept away. In another case Wellman

[1] For other methods described by Wellman see also U. S. Patents 1,323,383,
Dec. 2, 1919; 1,328,468, Jan. 20, 1920; 1,335,767, 1,335,769, 1,335,770, 1,335,771,
1,335,772, 1,335,773, and 1,335,774, April 6, 1920.
[2] U. S. Patent 1,347,567, 1,347,568, 1,347,661, July 27, 1920.

recommends scouring the cracking tube with superheated steam under
pressure after each cracking operation. The coke and tarry residuum
is thus swept out before it has become closely adherent to the walls of
the retort.

The apparatus used by **Trumble** [1] consists of a furnace A, Fig. 129,
in which is placed a heating coil. The heating coil communicates
with the interior of a vapor releaser B which is placed in a closed cham-
ber in open communication with the interior of the furnace. Vapors
from the vapor releaser are carried into a cracking chamber C in which
they are mixed with the hot gases of combustion and with superheated
steam which is primarily produced by a steam coil and nozzle located
in the bottom of the furnace A. Draft is produced in the various
portions by means of a suction blower D which delivers the combined
gases into a scrubber, in which the carbon, tar, etc., are removed, a con-
denser being provided for condensing the volatile products.

The primary heating coil consists of a number of pipes which pass
longitudinally through the furnace, and which are provided with end
connections so that they are connected in a single series, the oil entering
this series through an inlet pipe H and leaving it through an outlet
pipe K. The pipe K extends up and connects into the vapor releaser B,
the oil from the coil passing downwardly through the interior of the
vapor releaser. This vapor releaser consists of a metal shell in the
center of which is located a vapor pipe M having perforations in it.
The vapor pipe is provided with a series of spreaders which tend to
force the down flowing oil against the inner walls of the shell, and at the
same time to protect the perforations from the down flowing oil, and
to provide a series of pockets in which the vapor may cool. The in-
terior of the chamber B is connected to the chamber C by means of a
mixing passage and the pipe M projects into this passage and is provided
with a vaporizer on its end. This vaporizer is provided with holes
so that the vapor from the vapor releaser is thoroughly mixed with the
hot products of combustion from the burner and with steam. The
cracking chamber C is provided with a conical bottom which has an
outlet pipe. The vapor releaser B also has a similarly shaped bottom
and is likewise provided with an outlet pipe.

Porter and **Rider** [2] state that if a fuel liquid, such as a heavier hydrocarbon oil,
for example, kerosene, be subjected, when in a finely divided condition, to the di-
rect action of a naked flame for a properly limited short length of time, the liquid
fuel will be converted into a combustible vapor well adapted for use as fuel in an
internal combustion engine. They pass the finely divided liquid material into a

[1] U. S. Patent 1,304,125, May 20, 1919.
[2] U. S. Patent 1,064,086, June 10, 1913.

flame of sufficient extent and intensity to effect only a vaporization of the liquid material while it is present in the flame, so that the material emerges from the flame as vapor, the vapor being generated in the flame and passing out of it at high velocity, and given freedom for expansion.

J. E. Holmes [1] passes a mixture of oil (kerosene, or gas oil) and natural gas under pressure through a coil of pipe heated to a cracking temperature and then expands the reaction products adiabatically. It is said that the method is not attended with the difficulty of carbon deposit and that a sweet smelling gasoline is obtained.
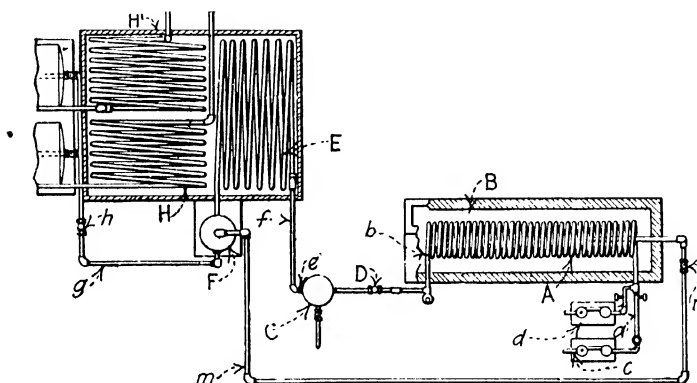
Fig. 130. — Holmes' method of cracking in the presence of natural gas.

In Fig. 130, a retort or heater A is heated by a suitable furnace B and consists of a coil of pipe. Connected with the terminals of this coil are conducting pipes a and b. The intake pipe a serves as a combined conducting and mixing conduit, in which the oil or distillate employed is commingled with natural gas, the oil and gas being forced through the pipe a to the coil A by means of pumps c and d, a meter being provided in the intake pipe for indicating the amount of the oil pumped to the coil, and gages being arranged in the branches of the intake pipe a leading from the respective pumps for indicating the pressures of the oil and gas. The mixture of oil and gas forced into the coil A, in the ratio of two volumes of gas to one volume of oil, is subjected, while under comparatively high pressure, to a high temperature. The pressure in the retort A is varied from 50 to 100 pounds per square inch, depending on the temperature, which is maintained at from 705° to 1100° F. (399°–593° C.), depending on the density of the oil to be cracked From the coil the vapors and gas discharge through the outlet pipe b and pass to an expansion and separator drum C, a pyrometer and a gage being provided in the pipe b to indicate the temperature and pressure. There is also a pressure regulator D, by means of which the pressure of the vapor and gas flowing to the expansion drum may be governed and the pressure of the vapor and gas within the drum regulated. The drum C consists of a cylindrical vessel having at its top an inlet, with which the pipe b is

[1] J. S. C. I. 1917, 1173A;   U. S. Patent 1,241,979, Oct. 2, 1917.

connected, and an outlet and having at its bottom a drain pipe. The latter has a controlling valve. The inlet and outlet are separated by a vertical baffle, so that the vapor and gas entering the expansion drum pass downward into the drum and are prevented from taking a direct outlet through the discharge connection. The vapor and gases passing into the drum are caused to expand under adiabatic conditions. This allows the heavier constituents to condense and precipitates the tar and coke. The lighter and more volatile constituents and gas remain in a gaseous state, owing to their high temperature, and discharge through the outlet.

The pressure in the retort A may vary from 50 to 100 pounds per square inch and the temperature from 750° to 1100° F. dependent upon the density of the oil to be cracked. The temperature and pressure maintained by direct heat is such, with relation to the specific gravity of the oil under treatment, as to effect
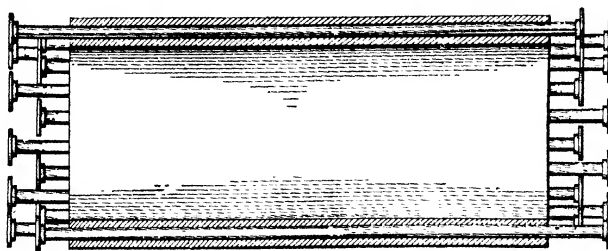
Fig. 131. — Pipe coil embedded in iron, proposed by J. L. Gray.

a thorough mixture of the vaporizable portions of the oil with the gas, and also to place the mixture in such condition that when raised to a higher temperature and pressure, it will be adapted for adiabatic expansion to precipitate all of the heavy constituents. This higher temperature and pressure is secured by the use of the pressure regulator D, which confines the mixture in the retort, by establishing a resistance to its discharge.

The vapors and gas discharged through the outlet e pass through a pipe f to a primary condensing coil E arranged within a cooled condensing chamber. From the coil the condensate and gas pass into a separator F, in which the noncondensable gas is separated from the condensate. The condensate discharges through a pipe g containing a controlling valve h, while the gas discharges through a pipe m having a controlling valve n, through which pipe the gas is conducted to the retort furnace B for the purpose of utilizing the gas as a fuel. The pipe g leads to a pair of stills for distilling off gasoline and kerosene. H and H' are condensers for these stills.

Whitaker and **Alexander** [1] state that the composition of the products obtained in making oil gas vary with the rate of oil feed and hence with the time factor. This variable is stated to be as important as the other three, temperature, pressure and concentration. Only by proper adjustment of all four, it is said, can maximum and minimum per cent

[1] J. Ind. Eng. Chem. 1915 (7), 484–95; Chem. Abs. 1915, 1842.

of the various constituents in the products formed by the decomposition of petroleum and petroleum distillates by heat be obtained.

Cowper-Coles [1] obtains motor fuel by passing oil vapors through small tubes heated to $926°$ C. ($1700°$ F.).

Davis [2] heats petroleum oils in retorts connected with a common header, withdraws the gases from the header and passes them through checker work heated to $1600°$ to $2000°$ F. ($871°$ to $1093°$ C.) in order to produce " fixed " illuminating gas.

C. B. Wade [3] describes a device for decomposing kerosene to yield gas for heating or lighting. Essentially it is a retort in which preheated kerosene is distilled and decomposed. The kerosene furnishes the heat supplied to the retort.

A device for protecting tubes which are to be used for cracking oil is proposed by **J. L. Gray.**[4] As shown in Fig. 131, the tubes comprising the cracking still are embedded in the wall of a hollow cast-iron cylinder. The thickness of the wall of the cylinder may be varied to suit special cases. It would appear that not only is the life of the tubes increased by this method, but a more constant cracking temperature also obtained. The horizontal tubes are connected at their ends by return bends, and by unscrewing these and the flanges, any tube or group of tubes may be readily removed for repair or cleaning. The apparatus is claimed to have considerable advantages over the older form of continuous coil pipe still.

[1] British Patent 27,945 (1906).
[2] U. S. Patent 1,058,660, Apr. 8, 1913.
[3] U. S Patent 1,304,225, May 20, 1919.
[4] U. S. Patent 1,331,909, Feb. 24, 1920.

CHAPTER XIV

TUBE CRACKING IN THE VAPOR PHASE — *Continued*

Hall's Process and Methods

Hall's method of producing gasoline from heavy distillates represents one of the few commercially promising vapor phase tube methods of making gasoline or motor spirit. Three of the main difficulties attending vapor-phase tube methods, viz., production of carbon deposit, accompanied by a large amount of waste gas and the consequent highly unsaturated character of the low boiling condensed product, have been attacked by Hall. His method of procedure in proposing to solve these problems constitutes the main portion of the text that follows.

Lomax[1] states that "Hall's process (for decomposing heavy oils to yield motor spirit, benzol and toluol) modified from time to time, as experience has been gained, is one, probably the most successful, of those being worked."[2]

Cracking with Subsequent Endothermic Reactions between the Hydrocarbons

Hall[3] believes that high temperature makes for high unsaturation, which has been a great objection to gasoline obtained by cracking. When, however, the temperature declines below a certain point, the conversion into motor spirit rapidly decreases. To just what extent unsaturated hydrocarbons are objectionable is subject, he believes, to a great difference of opinion. The general belief is that they are much more inclined to give a smoky exhaust, and to form carbon or soot deposit in the cylinder and on the plugs. Any large portion of unsaturated hydrocarbon in a cracked spirit is, however, extremely objectionable, according to Hall, for the reason that the resinous carbon " colloid," so common to cracked gasoline, exists largely, if not wholly, in the unsaturated portions. This, it is said, is the matter that gives cracked gasoline the varnish-like odor, that is frequently so noticeable. The color and odor is not wholly due to the resinous coloring matter,

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[1] " The Pyrogenesis of Hydrocarbons " by Lomax, Dunstan and Thole, Journal of the Society of Petroleum Technologists, 1916 (3), 36–120.
[2] In England.   [3] Hall, J. Inst. Petrol. Tech. 1915 (I), 147.

nor to the percentage of unsaturated compounds, and the color and odor vary greatly with the character of the oil that is used. Some fully saturated oils may give a deep colored cracked gasoline, and some quite unsaturated oils may give a very light colored product. The resinous substance appears to be a product of slow oxidation. It is a result of high temperature.

However, if the temperature is dropped to a point where these resinous products are not created, it is stated that the yield of gasoline may decrease to a point below that of profit. These conditions may be met, according to Hall, by hydrogenating the unsaturated bodies produced as a result of high temperature, but it is claimed that at the time of his observations (1915) this had proved altogether too expensive for commercial use.

A better way (Hall, *ibid.*) is to avoid the formation of the " varnish-forming " compounds by operating at comparatively low temperatures and then to combine the gases which are not readily condensed with the condensable vapor in a mechanical compressor at a slightly elevated temperature. Hall[1] sums up the various steps by which the result referred to is accomplished as follows:

1. Cracking an oil — (which may be crude, " gas," fuel, lamp or almost any distillate that in itself has a range of boiling temperatures that would not permit its use as a fuel in the ordinary automobile engine) — in a continuous tube of small size, one to three inches in diameter, and of sufficient length, at an average temperature of from $540°$ to $600°$ C. ($914°$–$1112°$ F.) and under pressure of about 75 pounds per square inch, with a rate of flow of oil in the pipe regulated to produce a maximum of cracking with a minimum of fixed or permanent gas consistent with economy of operation.

2. Expanding the product subsequent to the cracking operation by reducing the pressure.

3. Cooling the vapors and gases when in this expanded state and from them separating fractions which have relatively high boiling points.

4. Producing an endothermic chemical reaction between the gases and vapors, by compressing them under adiabatic conditions, in a mechanical compressor to a pressure from 100 to 125 pounds per square inch together with all the gas that has been produced along with all the spirit vapors that boil below the point of " cut," admitting these

[1] Hall, J. S. C. I. 1915, 1045; Chem. Abs. 1917, 2043; Chem. Abs. 1917, 3427; Chem. Abs. 1916, 2634; British Patents 6069, April 22, 1915; Int. Conv. May 11, 1914; 12,962, May 26, 1914; 437, January 7, 1914; 103,720, March 4, 1916; U. S. Patents 1,239,100, September 4, 1917; 1,239,099, September 4, 1917; 1,285,-136, November 19, 1918; Swedish Patent, 43,730, Mar. 6, 1918; U. S. Patent 1,175,910, March 14, 1916.

into the cylinder of the compressor at a temperature sufficiently high
so that they enter while in the shape of vapor and mist. The fixed
gas that has not been attached is separated after cooling subsequent
to the mechanical compression and is collected for other use. There
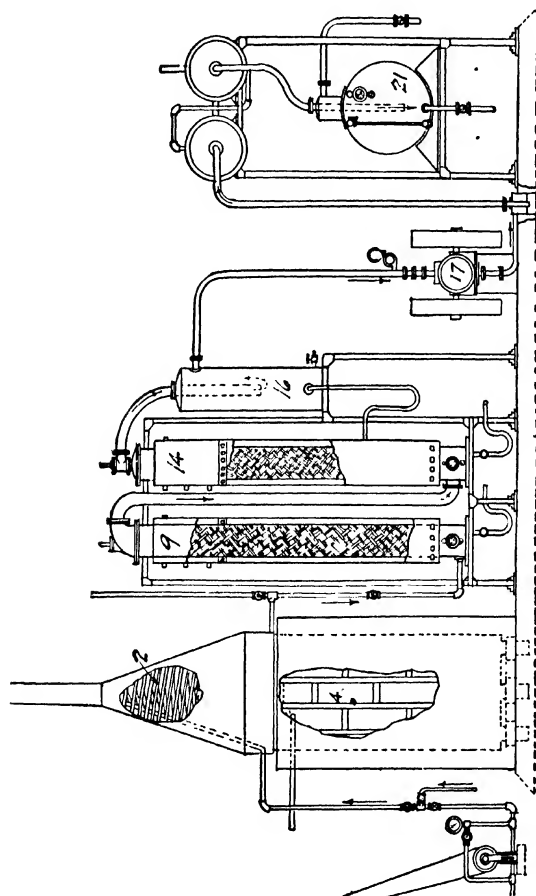
Fig. 132.

may be a small amount of heat radiated or otherwise lost from the
surface of the compressor to the outside atmosphere but no heat is
purposely taken away or added to the system.

5. Clarifying and deodorizing the product by extracting the yellow
resinous colloidal matter which it contains, by distilling it, in the pres-
ence of a small amount of fuller's earth.

Figure 132 shows the apparatus used, up to the condensation of the motor fuel.

In practice a crude oil or a distillate which may be a " gas oil " of about 0.860 specific gravity or a fuel oil of say 0.950 specific gravity or a low grade burning oil of about 0.82 specific gravity is selected. This oil is forced by means of a pump through a coil of 1″ or 1½″ pipe, 2, located above a furnace where it is preheated by the hot products of combustion. It is then passed through the cracking coil 4 heated by burners to an average temperature of from 540° to 600° C. (1004°–1112° F.) according to the oil used. The temperature of the gases and vapors conveyed in the tubes may be of somewhat lower temperature than that existing at the exterior of the tube, opposite the same point, varying with the rate of flow of the fluid in the coil and slightly higher at the bottom of the bends and slightly lower at the top. As an example, the oil is pumped through the cracking coil at about the rate of 50 to 70 gallons per hour. This rate will be varied with the quality of the oil used. The length of tubing of coil 4 is about 320 feet. The rate of flow and the length of coil mentioned are given, it is said, as examples of rate and length producing good results; the rate of flow may be increased or reduced by quite a considerable amount without greatly changing the result. The coil may be increased in length but if of 1-inch pipe could not be reduced much below the figure mentioned without changing the result. The cracking coil 4 is heated with gas or by the combustion of oil, coal or coke. Oil is partially cracked and there is produced a considerable amount of gas which would remain as permanent gas under ordinary conditions. From coil 4, the gases and cracked oil in the state of vapor pass in the direction of the arrow through a pipe which is fitted with a valve. This valve is used as the main throttle and governs the amount of oil passing through coil 4 and also governs the pressure maintained in that coil. A pressure of about 75 pounds per square inch maintained in coil 4 appears, it is said, to give the best results. After passing the throttle valve, the gases expand into the dephlegmator 9 fitted with an air jacket and filled with short pieces of pipe, in which the pressure is decreased from 75 pounds per square inch (the pressure within the coil C) down to about 10 pounds per square-inch or less and the temperature is reduced down to about 325° C. (617° F.). Carbon is thrown out in large quantities by the expansion of the gases and collects on the filling material in this and the succeeding dephlegmator.

The portions of oil not volatile at the temperature of about 325° C. (617° F.) condense in dephlegmator 9 and are extracted from the bottom in the form of a " heavy residue " of a gravity of about 1.0.

The more volatile portions pass on in the direction of the arrow and through a second dephlegmator where the temperature is reduced to the point at which it is desired to make the final " cut," usually about 180° C. (356° F.). The condensable portion is also extracted from the bottom of the second dephlegmator. The residue is termed " light residue." This is usually of a gravity of about 0.880 and is used as raw material for a second run through the cracking coil. The portion volatile at the temperature of the cut (for example 180° C.) (356° F.) accompanied by all of the gas is then passed through a separating tank (from which any liquid may return to dephlegmator 14) and without further cooling the vapors and gases are passed through the cylinder of a mechanical compressor 17 in which the pressure is raised, up to 100 or 125 pounds per square inch. In the cylinder of this compressor there is stated to be produced between the products an endothermic reaction, which is shown by a decrease in temperature at the exit as compared with the inlet or at any rate by a much less increase in temperature than would occur provided no endothermic chemical action took place. The product is then passed to coolers, and then to a receiver where the liquid collects, and the uncondensed gas is vented.

The product is said to be quite stable and of a yellow color and has a disagreeable varnish-like odor. It contains a material which, upon evaporation of the liquid, remains as a dark orange, non-drying substance, with a strong odor. This product accordingly could not well be used as a successful automobile fuel. It is clarified and rendered water white and its disagreeable odor removed by redistillation without the loss of its large fractions boiling at low temperature and without much change in its specific gravity. This is effected by agitating the spirit with about 10 per cent of its weight of fuller's earth, separating the spirit from the mineral matter and distilling it. Although this agitation removes, it is said, very little of the color (judging by appearances), when distilled the distillate is water white. The coloration and odor may be removed by direct distillation of the spirit from a mixture with fuller's earth or the clarifying of this crude yellow spirit may be effected by treatment with a small amount of sulphuric acid, according to Hall.

Concerning the " affixation " of the " wet " gases in the mechanical compressor, Hall [1] states that the

" amount of easily condensable fractions that are contained in a gas derived by cracking an oil are so small in proportion to the whole, that simply its *addition* would not constitute any very considerable gain. We have scrubbed such gases in

[1] In a paper read before the Institution of Petroleum Technologists, 1915, pp. 147–166.

the most effective manner, obtained the condensable portion, and calculated to
what extent it would increase the yield from its simple addition. This has
amounted to from only 5 to 8 per cent against an average increase of fully 33 per
cent by its *attachment* in the manner which has been adopted; but the most im-
portant point is that this 33 per cent addition is *all* of the lightest gravity and
lowest-boiling fractions, and makes an excellent working motor spirit out of one
that would otherwise be of little value.[1] "

"This 33 per cent of increased light fractions *is not gas in solution.* The
proportionate increase is sufficient to disprove such an assumption. But there are
many other proofs, perhaps the most important being that gas held simply by
solution is largely dispelled by distillation. Yet this spirit can be several times
distilled with very little loss of the fractions boiling at the lowest points, and this,
when the condensation is at a normal temperature, conducted into an open vessel
with no pressure."

It is apparently the easily condensable gases, "wet" gases, as Hall
calls them, which are capable of combining with the liquid unsaturated
hydrocarbons boiling below 200° C. (392° F.) produced together with
liquid saturated hydrocarbons.

When certain kinds of oils are used, the amount of gas produced in
the operation is in excess of that which will combine with the liquid
unsaturated hydrocarbons at an elevated temperature in the compres-
sion and subsequent condensation. Or, some of the gas produced may
be "dry" gas, that is, gas which is not easy to condense, e.g., ethane or
methane, and which does not easily combine with the liquid unsaturated
hydrocarbons. A method of utilizing these gases consists in charging
them into benzol or toluol or a mixture of benzol and toluol.[2] When
the operation is properly carried out, the resulting liquid is said to be a
good motor fuel.

The receiver beyond the condenser is partly filled with benzol, toluol or a
mixture of these, through which the products of the process pass, or the benzol,
toluol or mixture may be admitted into the receiver simultaneously with the
products and in such a manner that these products become intimately mixed
and under the pressure that is usually maintained in the receiver tank. The ex-
cess of gas obtained is to a considerable extent absorbed by the benzol and toluol,
thereby decreasing the amount of unattached gases passing from the receiver and
giving a product with a very low initial boiling point. The boiling point of or-
dinary benzol is approximately 80° C. (176° F.), and that of toluol approximately
110° C. (230° F.), yet when these liquids are treated in the manner described, the
initial boiling point of the mixture is found to be approximately 25° C. (77° F.)
to 35° C. (95° F.). In this manner the objections to benzol and toluol as a motor
fuel are largely overcome, it is said, by imparting to them an initial boiling point
as low as or lower than that of gasoline, and at the same time saving much gas
that would ordinarily not be recovered.

[1] Hall apparently means the percentage of *volume* increase in yield from the
action of pressure and heat on the partly unsaturated gases and vapors.

[2] Hall, J. S. C. I. 1915, 346 and 1045; British Patents 12,962, May 26, 1914,
and 437, January 7, 1914.

Instead of expanding the reaction products to a low temperature after leaving the " converter " or " cracker," **Hall**,[1] in one phase of his work, cools the gases and vapors partly by air cooling and finally by water cooling, under practically the same pressure as exists in the converter. The products first pass through air cooled condensers and separators to remove material boiling above 200° C. (392° F.) and then through a condenser to liquefy the very volatile products. In this particular procedure no mechanical compressor is used.

However, it is considered decidedly advantageous to lower the pressure [2] as soon as the products leave the converter, in order to assist in separating free carbon and tarry materials. For example, if the pressure in the cracking tubes or converter is 70 pounds per square inch and the reaction temperature 550° to 650° C. (1022°–1202° F.) the pressure is lowered to not much more than atmospheric and the temperature to about 200° C. (392° F.). In Fig. 133 this cooling takes place in the air condensers B, B' and the expansion takes place through the valve C. Products boiling above 200° C. (392° F.) are separated in the chambers attached to the air cooled condensers. The products boiling below 200° C. (392° F.) represent the hydrocarbons resulting from the cracking operation. These may be divided (Hall (*loc. cit.*)) into two classes, first, gases, and secondly, liquids. The liquids are largely of the olefin series and as such are not recommended as motor fuels; but by compressing both together in a mechanical compressor up to a pressure of 125 pounds per square inch and at a temperature of about 180 to 200° C. (356 to 392° F.) and then cooling together under this pressure, it is stated[3] that the gases and unsaturated liquid hydrocarbons undergo a combination.

By interposing a chamber containing fuller's earth, dehydrated bauxite or infusorial earth between the compressor and pressure condenser (see Fig 133)[4] the low boiling point products pass through the mass of clarifying material and the ultimate product is said to be free from color and objectionable odor.

The gasoline produced by cracking in tubes, subsequent expansion and compression of the vapors and gases volatile below 200° C. (392° F). in a mechanical compressor, while those volatile products are in the form of gases and mists (i.e., at a temperature of about 180° C.) is said[5] to

[1] Chem. Abs. 1918, 222; J. S. C. I. 1915, 216; U. S. Patent 1,242,795, Oct. 9, 1917; British Patent 24,491, Oct 28, 1913; J. S. C. I. 1914, 583; French Patent 467,381 (1914).

[2] Hall, Chem Abs. 1918, 221; U. S. Patent 1,242,796, Oct. 9, 1917.

[3] Hall, *loc. cit.*

[4] Hall, J. S. C. I. 1915, 346; British Patents 7282, March 23, 1914, and 24,491, Oct. 28, 1913.

[5] Hall, U. S. Patents 1,239,099 and 1,239,100, September 4, 1917.
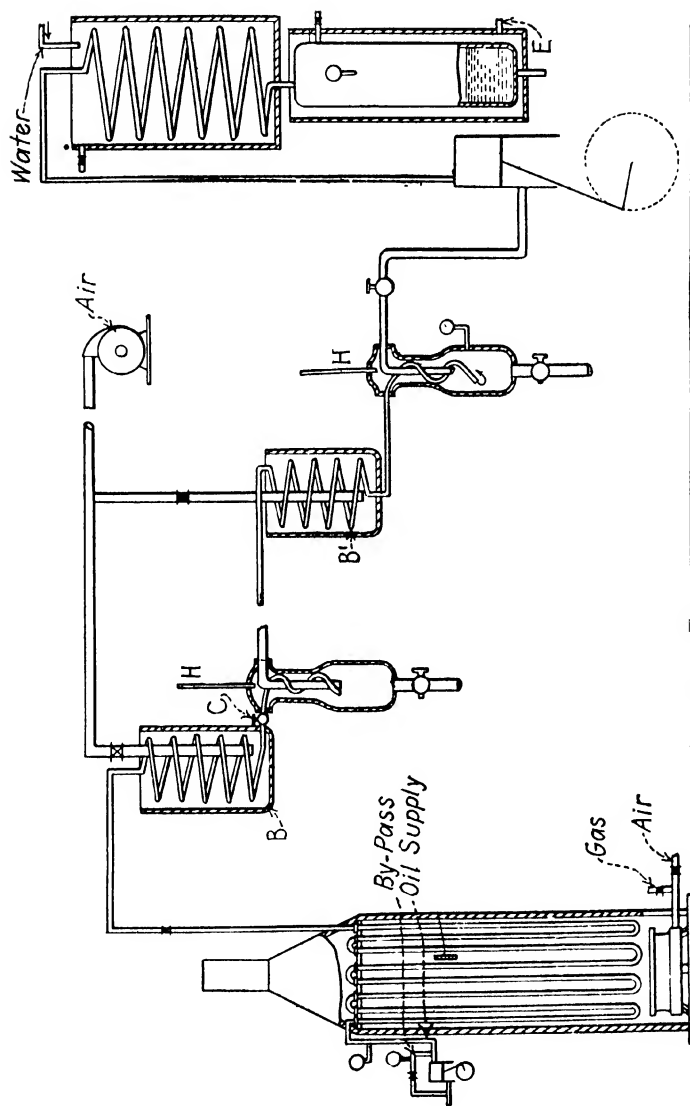
Fig. 133.

be free from liability to pre-ignite, and therefore when used as a motor
fuel in an ordinary automobile engine "knocking" does not occur,
even with the spark advanced. The mixture of air and the fuel ignites
very readily, but the flame does not propagate itself through the mix-
ture of air and vapors as rapidly as with ordinary gasoline. In other
words it is slow-burning, hence its freedom from "knocking." On
account of the high percentage of low volatile contents, it can be cut
at 180° C. (356° F.) or higher. Its large fractions volatile at low tem-
perature have been found to carry complete combustion to the fractions
volatile only at the highest temperatures, a considerably increased
mileage per gallon consumed being the result.

The low flash point and low initial boiling point give, in an engine
run on the fuel, great ease in starting in cold weather, and flexibility
(quickness of acceleration). It has been found, it is stated, that its
great flexibility and ease of starting can be obtained with this fuel when
"cut" at 180° C. (356° F.) and of specific gravity 0.760 as can be
obtained with a straight gasoline of specific gravity 0.730 "cut" at
160° C. (320° F.).

Hall prefers to speak of his product as "fuel" rather than as
"spirit," because in the minds of many people the latter term indicates
products all distilling below about 120° C. (248° F.), and in this liquid
there is a considerable fraction distilling above this temperature, the use
of which, in a motor-car engine, supposedly is rendered possible by
the presence of constituents of lower boiling point than any present
in ordinary gasoline, or by the larger percentages volatile at 120° C.
(248° F.).

The condensation together under pressure of the heavier hydro-
carbon gases with the vapors of the lighter hydrocarbon liquids, gives
a product from which the gases show but little tendency to escape at
ordinary temperatures. When the liquid is drawn from the collecting
tank the escape of the less easily liquefied gases and expansion cause
the liquid to be cooled down below the freezing point of water, and when
this liquid is brought into a warm room it shows beads of escaping gas
for a short time, but this soon ceases and the liquid shows no effer-
vescence such apparently as would occur had the gases been merely
dissolved in a cool liquid hydrocarbon under pressure. On distilling
the motor fuel it is found, according to Hall, that from 9 to 11 per cent'
of its constituents pass off as gases and vapors which are not recon-
densed under ordinary conditions, and that the presence of these gives
the fuel a higher vapor pressure, which is invaluable in the starting of
the engine in cold weather.

The following comparison of the vapor pressure of the fuel with that of
" Pratt's No. 1 Perfection Gasoline " is given:

Vapor pressure in inches of mercury

Temperature		Hall's Fuel	Pratt's No. 1 Gasoline
° C.	° F.		
12.8	53	2.15	0.7
15.5	59	3.8	1.4
18.3	64	5.8	2 6
21.1	69	7.8	3.6
23 9	73	9.8	4.8
26.7	78	12 0	5 9
29 4	84	14.2	7.1
32 3	89	16 3	8.25
35 0	95	18 4	9.3
37 8	98	20 6	10 5

The vapor pressure of Hall's fuel may be taken as about double that of
Pratt's. The loss in volume and increase in specific gravity on exposure to air
are not as high as might be expected from the vapor pressure. Comparative ex-
periments with No. 1 Pratt's gasoline gave the following results:

Evaporation from a surface of 21 square inches at ordinary temperature

Time exposed	Hall's fuel	Pratt's No. 1
1½ hours	14 6 %	13 9 %
3 hours	18 2	19.4
4½ hours	21 0	25 2

Three determinations of calorific value in each of which 10 grams of the fuel
were consumed were made, the temperature readings being closely concordant and
the calorific value (per 10 grams) calculated from them being:

Hall's fuel

		Gross	Net
1		10,462 calories	9,841 calories
2		10,560 "	9,840 "
3		10,493 "	9,873 "
Mean		10,505 "	9,884.7 "
		18,906.6 B.t.u.	17,790 B.t.u.

Pratt's No. 1 spirit

1		10,330 calories	9,709 calories
2		10,145 "	9,463 "
3		10,132 "	9,226 "
Mean		10,202.3 "	9,466 "
		18,366 B.t.u.	17,046.3 B t.u.

While figures given for Pratt's spirit by several observers are higher than these
determinations, the latter are comparative and show the calorific value of the
product produced in Hall's process to be slightly higher than that of Pratt's No. 1
Gasoline (about 3 per cent higher in this test), a result borne out by bench tests
made with the following comparative results:

Although the bench test was made on a cold morning, the engine, it is said, started well with the fuel, and showed perfectly smooth running even with reduced load.

The measurements for five sets of tests are summarized below:

		Hall's Fuel	Pratt's No. 1
1. Full load test:			
Revolutions per minute	 1000		1000
Kilowatts, load.		2.93	2.99
Gallons per hour	. . . .	0.69	0.85
Gallons per kilowatt hour		0.236	0.284
2. Acceleration test:			
Revolutions per minute	 1300		1300
Kilowatts, load.	. . . .	2 36	2 37
Gallons per hour	. . . .	0 76	1 12
Gallons per kilowatt hour	. . . .	0 3222	0.473
3. Reduced load test:			
Revolutions per minute	 1000		1000
Kilowatts, load.	. . . .	Nil.	0 40,
Gallons per hour	. . . .	0 52	0.67
4. Test at normal speed:			
Revolutions per minute	 1000		1000
Horse power	. . . .	14.5	13
Gallons per hour	.	1 41	1.67
Gallons per horse power hour	. .	0 097	0.128
5. Re-test at increased speed:			
Revolutions per minute	 1300		1300
Horse power	. . . .	17	17
Gallons per hour	. . . .	1 66	2 02
Gallons per horse-power hour .		0 098	0 120

The exhaust from the engine when running with the cracked gasoline was very free from smoke and had no objectionable odor, while Pratt's No 1 produced both smoke and odor. It will be noticed that the cracked product showed the greatest economy over ordinary gasoline in the acceleration test and reduced load test, this presumably being due to the rapidity with which the fuel forms the explosive mixture.

An attempt was made to analytically determine the nature and proportions of the permanent gases escaping condensation and also those liquefied, absorbed or combined with the condensing spirit.

Using an American " petrolite " oil with a specific gravity of 0.815 it was found that on the average 12 cubic feet of permanent gas were formed per gallon of oil subjected to the cracking and condensing process and left the apparatus as gas after the compression and condensing had taken place. Samples of the escaping gas were analyzed and were found to have the following composition:

Ethylene. 31.1
Ethane. 25.4
Methane. 34.6
Hydrogen. 8.9
                                                            _____
                                                             100.0

and its calorific value as determined in the Junker's calorimeter was
1442.6 British thermal units per cubic foot.

A portion of the finished fuel from the run mentioned above after
being drawn off and allowed to stand until signs of " beading " had
ceased and the liquid had been allowed to be warmed up to the tem-
perature of 16° C. (60° F.), was distilled up to 150° C. (302° F.) and
the gases and vapors escaping condensation by water cooling were
collected and analyzed and were found to consist of:

> Unsaturated hydrocarbons........ .   73.4
> Saturated hydrocarbons...............   26.5

The gas left after absorption by fuming sulphuric acid, on exploding
with oxygen, yielded carbon dioxide and water vapor in the ratio of
3 to 4 which points to its being propane or a mixture of butane, propane
and ethane, while the whole gas on explosion with oxygen gave carbon
dioxide and water vapor in the ratio by volume of 5 to 4.1 which points
to the unsaturated hydrocarbons consisting (in part) of higher members
of the acetylene series, a view supported it is said, by the original fuel
giving a heavy precipitate with mercuric chloride.

A portion of the original fuel from the same run, when subjected to
ultimate analysis, gives as figures:

> Carbon................   85.9
> Hydrogen..............   12.76

a carbon-hydrogen ratio of 6.73 to 1, the carbon being in excess of that
required by either the saturated or ethylene series and pointing to the
motor fuel being a mixture of these with an even less saturated com-
pound. The bromine absorption given by the fraction of the fuel
distilled up to 150° C. (302° F.) is 101.8 but after acid treatment and
steam distillation the distillate gives a bromine absorption number of
only 44.7, while the original motor fuel produced in some of the runs
gave a bromine absorption number as high as 150. This points to the
light fractions containing highly unsaturated hydrocarbons. The
product appears, it is stated, always to contain considerable amounts
of unsaturated hydrocarbons, and to possess the valuable properties of
slow burning, quick igniting, and the absence of knocking.

The Production of Benzol, Toluol, etc.

Lomax[1] states that the benzene-toluene produced by the Hall
process contains only minute traces of non-aromatic bodies and the
toluene produced is as easily nitrated as coal-tar toluene.

[1] In the Pyrogenesis of Hydrocarbons, by **Lomax, Dunstan** and **Thole**, Journ.
Institution Petroleum Technologists, 1916 [3], pp. 36–120.

A point to consider is the difference in the mode of operation of Hall's process when he produces benzene and toluene from the case where gasoline is desired.

In the production of benzene and toluene, a considerable amount of gas is generated. When it is a question of producing aromatic hydrocarbons, rather than obtaining motor spirit, the mechanical compression of the gases produced, together with the vaporized liquid hydrocarbons boiling below 200° C. (392° F.), is not required.[1]

The process consists in subjecting the oil to a partial cracking by forcing it under pressure at a high rate of flow through small tubes heated to a sufficiently high temperature to produce partial cracking. The oil is vaporized to such an extent that the speed of the vapors and gases through the tubes is increased very largely, and then, while they are no longer subjected to external heating, the velocity of the vapors and gases is sufficiently reduced, thereby transforming the energy in the form of velocity, save the initial velocity, into heat of a superheating character which completes the cracking operation without converting the vapors into permanent gas. The oil is passed at high speed through small tubes of approximately one inch diameter under a pressure of approximately 75 pounds (or more) per square inch and at a temperature of the vapors inside the pipe of from 550° C. (1022° F.) to 700° C. (1292° F.), depending upon the product to be obtained and the oil treated. The oil is vaporized in the tubing to such an extent that the speed of the vapors becomes from 5000 feet per minute upward, the amount of feed being so large and the temperature so low that only a partial cracking is effected in these tubes. The high rate of flow and incomplete cracking prevents, it is said, any material deposit of carbonaceous matter in the tubes. The gases and vapors are then expanded into a much larger tube, say of from 12 inches to 16 inches in diameter (and which may be 8 to 11 feet in height) in one or more stages, by impinging against baffles or filling in order to suddenly reduce the velocity to an enormous extent, thereby transforming the mechanical energy of the gases and vapors in the form of velocity into heat. The temperature of the vapors and gases in the large tube is consequently raised without any extraneous heat being applied. The cracking operation is thus completed in this large tube. As the walls of this large tube are cooler than the center of the mass of vapors passing into it not much decomposition of the vapors into permanent gas takes place at this point.

In converting the product of the cracking operation into hydrocar-

[1] Hall, J. S. C. I. 1916, 626; Chem. Abs. 1916, 1929; U. S. Patent 1,194,289, August 8, 1916; British Patent 1594, Feb. 1, 1915

bons of the aromatic series a compressor such as that shown in Fig. 132 is not necessary. (In producing motor spirit a compressor is required, as without it there is not obtained in the final product a sufficient
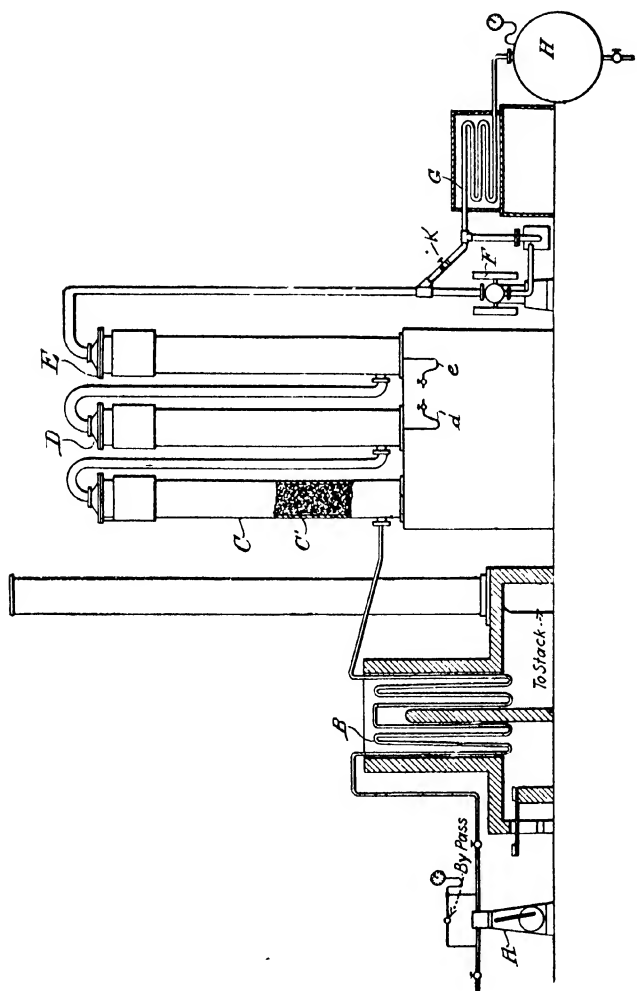
Fig. 134.

amount of low boiling fractions.) In treating the oil for the purpose of conversion into members of the aromatic series, the oil in the tube constituting the decomposing retort or " converter " is subjected to a higher temperature than in the production of motor fuel (about 650° to

700° C. (1202 to 1292° F.)) and a correspondingly higher pressure is produced. This temperature depends to some extent on the character of the oil treated, oils such as those of Mexico, California and Persia requiring lower temperatures to obtain the same results than do oils like Pennsylvania kerosene. In operating at high temperatures there will be no need for a throttle valve such as that beyond the converter in the methods previously described, since the necessary pressure of 75 pounds and above is obtained entirely from the amount of oil fed in and the expansion of the vapors. It has been found that when running at say 700° C. (1292° F.) and feeding the oil at the rate of 90 gallons per hour through a 1-inch pipe, the expansion is so great that the desired pressure is obtained without any throttling.

In practicing the process for the conversion into aromatics there is produced much more fixed gas than is produced when the process is operated for the production of motor spirit, on account of the higher temperature used. The product does not consist entirely of members of the aromatic series, and subsequent distillation to separate the benzene, toluene and xylene from the paraffins is necessary.

By only partially cracking the oil in the heated tubes and by producing a rise in temperature and effecting as large an amount of the cracking as possible beyond the influence of external heat, the production of large amounts of fixed gas (which are of course of a less value than the condensable spirit) is largely prevented. If the cracking were all done in the heated tubes, the assertion is made that the permanent gas produced would be much greater than is produced when a considerable amount of the cracking is effected at a point beyond the influence of the external heat. The light vapors never being exposed to a higher temperature than that of their production are not decomposed into fixed gas by superheating.

The mechanical energy in the form of velocity of the gases is largely converted into heat which superheats the whole in a somewhat similar manner to that in which steam is superheated in a throttling calorimeter. In Fig. 134 A is a pump which is operated at a speed suitable for forcing the oil to be treated at a high rate of flow into a converter B to a temperature suited to produce partial cracking of the oil and under a pressure of 50 to 75 pounds (or more) per square inch. The vapors and gases produced in the converter B, partly on account of the expansion produced, pass at a very high speed into a very much larger vertical pipe or column C where the pressure falls to 1 or 2 pounds per square inch, this column being provided with baffles or suitable filling material for reducing the velocity of the vapors and gases suddenly to a very large extent. The vapors and gases are then led through dephlegmators D and E from which the heavy and light residues are removed by pipes d and e. The vapors and gases from E pass directly to the condenser G, through the valved pipe K.

The Use of Nickel as Catalyst

Hall,[1] commenting on the use of hydrogen or hydrogen-containing gases in the cracking of oils, states that water is of no use as a hydro-

[1] In the J. Inst. Petrol. Tech. 1915, 147–166.

genating agent, even in the presence of a nickel catalyst. He also contends [1] that the use of hydrogen in this connection is very expensive and that the nitrogen, carbon monoxide and carbon dioxide content of producer or water gas presents difficulties. In one phase of his work he avoids the use of hydrogen or steam and states (*ibid.*) that the decomposition of the oil itself furnishes hydrogen in a "nascent" condition, which combines with the unsaturated hydrocarbons produced.
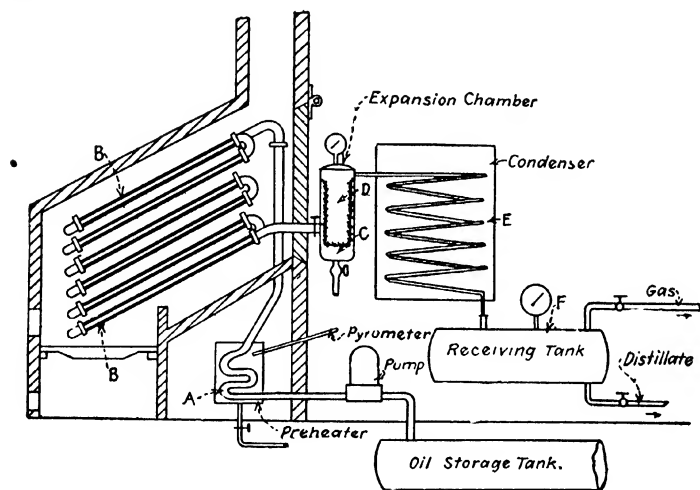
Fig. 135.

The heavy hydrocarbon is subjected to heat and pressure in the presence of a catalyst capable of effecting the hydrogenation of unsaturated hydrocarbons. The products are allowed to expand and deposit carbon, and the residual products are cooled to produce by condensation a liquid hydrocarbon containing less carbon than the original hydrocarbon, and adapted for use in high speed internal combustion engines. If the hydrocarbon oil is heated under a moderate pressure, say a pressure of about 5 atmospheres, to a temperature of upward of 600° C. (1112° F.) in the presence of the catalyst, and in the absence of steam or any extraneous source of hydrogen, a conversion of the oil takes place, the oil being partially decomposed and gases set free. These gases are in turn decomposed by the heated catalyst with liberation of hydrogen which in a nascent state is, to a considerable extent, it is maintained, affixed to the condensable portion of the decomposed hydro-

[1] J. S. C. I. 1914, 1149; U. S. Patent 1,175,909, March 14, 1916. See also British Patent 17,121, July 25, 1913; Chem. Abs. 1915, 375.

carbon oil. The catalysts used are the metals, or oxides of the metals, nickel, cobalt, silver, palladium, chromium or manganese.

The apparatus includes a preheater A, Fig. 135, for raising the temperature of the oil and to some extent volatilizing it before it enters the tubular converter B, so that the gas may be produced at as early a stage in the process as possible. The converter B, Fig. 135, is a serpentine inclined metallic tube so arranged that the circulation is through the top section, then down and through the next, and so on to the bottom, the exposure being at first to the lowest temperature, which is at the top, and gradually increasing toward the bottom. In the tubular elements of the converter is placed the catalytic material in the form of rods which rest in contact with the heated walls of the tube. From the converter B the products are passed into an expansion chamber C where their temperature is somewhat reduced. The expansion chamber C is provided with a metallic gauze screen D, of conical shape, which will collect and extract any loose carbon that may be set free (it is found that the carbon is most readily deposited at the point where expansion occurs and to the greatest extent if the pressure be suddenly reduced from that in the converter (about 5 atmospheres) down to atmospheric pressure).

It is to be noted that the pressure of the vapors drops materially in passing from the converter B to the chamber C This drop in pressure appears to aid in the deposition of free carbon. The gases and vapors produced by the decomposition of the oil flow rather rapidly through the converter tubes, and since the cross section of the tubes is small, owing to the fact that the metal rod takes up quite a large part of the space, the current of gases and vapors flowing through the tubes carry along the free carbon, or soot-like material. Consequently not much of this will deposit within the retort. After the pressure falls, and the gases enter the larger chamber C, most all the free carbon deposits in the expansion chamber C, and on the gauze member D. Tarry matters are likewise separated in the chamber C. From the expansion chamber C the products are passed through a cooling condenser E and into a receiving tank F from which can be extracted any fixed gases that have not combined with the condensable portions The condensate is found to be a different product from the oil started with. It has a much lower specific gravity and boiling point and when redistilled and fractionated yields a large portion of volatile spirit adapted for use in automobiles For instance if the raw material used be " gas oil " (a refinery distillate having a boiling point above the boiling points of gasoline and burning oil) it will yield from 50 to 70 per cent of a fuel of a specific gravity of about 0.765 with a boiling point which is lower than that of commercial gasoline. The product of this process also contains a proportion of unsaturated hydrocarbons. The quantity of unsaturated hydrocarbons may vary more or less, but is always rather small. It is not necessary to redistill the condensate, as the fractionation can be effected by a dephlegmator situated between the converter and the condenser.

Steam was used by Hall with oil vapors in the presence of nickel [1] in an apparatus somewhat similar in principle to a producer gas converter (see Fig. 136). A mixture of heavy hydrocarbon oil and steam was passed through a highly heated chamber with restricted spacings

[1] J. S. C. I. 1918, 330A; U. S. Patent 1,261,930, Apr. 9, 1918.

so that its passage is retarded to an extent sufficient to create a considerable pressure, about 150 pounds to the square inch. In passing this mixture through the heated chamber, the whole mixture becomes vaporized and a considerable amount of carbon is deposited on the walls or surfaces which obstructs the passage of the vaporized material While the relative proportions of oil and water may be varied more or less, good results are said to be secured if about one pound of water is employed for each two or two and one-half pounds of oil.

In Fig. 136, *A* is a receptacle, which is divided by a screen into receiving and converting chambers, *B* and *C*. The vessel, *A*, is enclosed by a casing which retains the heat and affords a heating chamber, *D*, below the receptacle. In the heating chamber is located a heating burner The oil to be converted is discharged under pressure into the receiving chamber through a pipe communicating with a pump, and the water which is to be mixed with the oil is supplied to the receiving chamber in the form of steam forced into the chamber The converting chamber, *C*, is partly or wholly filled with a metal in small pieces which by being more or less compacted together, serve to obstruct the flow of the hydrocarbon through the converting chamber, and produce back pressure, and these small pieces of metal afford numerous surfaces on which a portion of the carbon in the vaporized mixture is deposited in solid form. These particles of metal are in the

Fig. 136.

form of nickel balls or cubes, as nickel neither oxidizes nor carbonizes, it is said, at the temperature (about 600° C. (1112° F.)), which is employed.
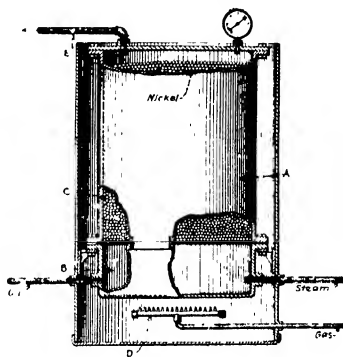
A series of " decarbonizers " or converters such as that shown in Fig. 136 are so arranged that they can be connected and oil passed from one to another, through a pipe, *E*, communicating with the converting chamber *C*, to a chamber corresponding to the receiving chamber, *B*, of another converter, and thus the mixture may be successively treated to " withdraw any desired amount of carbon."

In thus passing the liquid hydrocarbon through a series of these converters a considerable amount of carbon is deposited in solid form on the surfaces of the fragments or small pieces of metal with which the converting chambers are supplied, and the process may be carried on until the particles of metal in the converting chamber become so clogged with carbon that it will be necessary to throw it out of operation for cleaning which may be done simply by flooding with steam or water, as the solid carbon is in the form of loose flakes. Thus in using a series of these converters the connections may be such that some of them may be cut out, for the purpose of cleaning, while the others may be continued in operation

The hydrocarbon spirit produced is of a lower specific gravity and lower boiling point than the original hydrocarbon liquid before treatment, contains compounds of the ethylene or olefin series, although before treatment the liquid hydrocarbon was composed principally of members of the paraffin series. This

converted hydrocarbon spirit is said to be suitable for use in internal combustion engines.

The rate of flow of the vaporized oil and water through the mass of catalytic metal is such as to give a pressure of about 150 pounds per square inch, at a temperature of 600° C. (1112° F.). The oil vapor and steam may be in contact · with the nickel for about two to three minutes, giving good results.

The mineral oil operated upon may be a crude California oil, of a specific gravity of about 0.955, although other oils such as crude Pennsylvania, Ohio, Canadian, Texas oils, or stripped oils may be employed with good results.

It is remarked that nickel used in this connection has a very different effect from that which would be produced if metal were employed, which would be oxidizable under the existing conditions, for example iron. At the temperature stated, iron will decompose steam, in the presence of oil vapor, to produce an oxide of iron, and some free hydrogen will be produced. In such a process, however, the pieces of iron would soon become coated with a layer of iron oxide, which would prevent further action of the iron and steam upon each other. With nickel, however, it is observed that the metal does not become oxidized in the presence of oil vapor.

Miscellaneous Methods

Hall [1] produces motor spirit by passing the kerosene fraction boiling up to about 220° C. (428° F.) from which the gasoline has been removed, between minute interstices under very high pressure, e.g., 1000 to 3000 pounds per square inch in the presence of hydrogen, coal gas or other gas containing free hydrogen or a hydrocarbon gas, e.g., ethylene or oil gas, and at a temperature not above the lowest boiling point of the liquid, e.g., 100° to 120° C. (212°–248° F.). By this means, it is noted, there results a combination of the gas and the liquid hydrocarbon causing a certain amount of hydrogenation of the latter, the result being a considerable lowering of the flash point of the liquid hydrocarbon and an alteration of the odor. In order to produce this combination of the gas and oil a homogenizer may be used of the kind used in homogenizing milk consisting of a series of metal disks or plugs between or through which the liquid is forced in the presence of gas. The metal disks or plugs are made of nickel and are very finely grooved, i.e., provided with mere scratch marks. The gas employed may be hydrogen, or any coal gas containing hydrogen, or hydrocarbon gas such as oil gas or acetylene. The product obtained is distinguished by its much lower flash point than the fraction of kerosene having this

[1] Chem. Abs. 1917, 2043; British Patent 103,720, March 4, 1916; see also J. S. C. I. 1917, 127; French Patent 481,066, Feb. 25, 1916.

boiling range, also by the loss of the kerosene or paraffin odor and the production of a new odor and a liveliness of the fuel not possessed by kerosene when used in a high speed internal combustion engine. One volume of liquid is said to take up more than one volume of gas.

Hall [1] manufactures a fuel suitable for use in high-speed internal combustion engines which consists of equal parts of an uncracked saturated hydrocarbon of the paraffin series boiling from 140° to 230° C. (284° 446° F.), and a partly unsaturated hydrocarbon spirit produced by cracking. Hall states that the uncracked oil alone is objectionable as motor fuel and that owing to the high flash and boiling points an engine cannot be started on such fuel from the cold, and that this fuel is not as responsive to the throttle as gasoline. It is also stated that cracked spirits alone are not wholly suitable owing to their tendency to form gummy products of oxidation. By mixing the less volatile, saturated oil with the cracked spirit which is partly unsaturated and which contains a large proportion of very volatile hydrocarbons, Hall claims a fuel is produced almost free from the "gumming" tendency and free from the liability to knocking of the less volatile saturated oils. [2]

According to **T. T. Gray** [3] the Hall process is being used commercially in England and America for the production of motor spirit.

[1] J. S. C. I. 1917, 862; British Patent 106,876, June 16, 1915.

[2] See also Hall in chapters on Alcohol as Motor Fuel and Benzol as Motor Fuel and Refining Methods.

[3] Industrial Chemistry by Rogers, 3d Ed., D. Van Nostrand Co., New York, 1920, p. 630.

CHAPTER XV

TUBE CRACKING IN THE VAPOR PHASE — *Continued*

The Rittman Process

The Rittman process probably had its inception in certain investigations carried out by **Whitaker** and **Rittman** [1] in the thermolytic treatment of heavy oils with a view to increasing the illuminating power of carbureted water gas. It was found that good results were obtained by having high temperatures and low pressure in the cracking zone. The study of the physical and chemical conditions obtaining when petroleum is subjected in this way to high temperatures for the production of oil gas formed a natural preamble to an extensive study of the optimum conditions for decomposing petroleum less profoundly than in the production of oil gas, that is, for the production of low boiling hydrocarbons suitable as naphtha and gasoline.

At about this time the outbreak of the War created economic conditions which stimulated investigations to determine the sources, actual and potential, of benzol and toluol in the United States.

Rittman pursued his work at the Bureau of Mines, where the subject was investigated with customary thoroughness, with a view not only to decompose petroleum to yield gasoline hydrocarbons but also to produce aromatic hydrocarbons.

Special emphasis was laid upon the maintenance of a single gas phase in the cracking tubes; and the nature of the reactions that take place when gasified oils are submitted to interrelated conditions of temperature, pressure and time of reaction was studied in a most exhaustive manner. Inasmuch as the temperature could be varied independently of the pressure, owing to the absence of the liquid phase, it was found that the method finally adopted was sufficiently elastic to permit of the production of either gasoline hydrocarbons or aromatic oils.

Rittman's method [2] is stated to consist essentially in suddenly gasifying the material to be treated, cracking the gasified material in

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[1] Thermal Reactions in Carbureting Water Gas, J. Ind. Eng. Chem. 1914, 383–392, 472–479; J. S. C. I. 1914, 682.

[2] J. S. C. I. 1916, 1101; British Patents 9162, June 22, 1915 and 9163, June 22, 1915.

the absence of any liquid and under a pressure of at least six atmospheres and condensing resulting hydrocarbons that will condense at a temperature above 30° C. (86° F.). Emphasis is laid upon the fact that the process is a single phase one, i.e., that it is strictly a gas-phase process. Since in one phase systems the pressure may be held constant and the temperature varied and vice versa, it is stated that this cracking process is more elastic in its possibilities than any two phase process.

In the cracking operation, a large number of gases and vapors are formed, ranging from hydrogen to hydrocarbons having boiling points the same or even higher than those in the materials treated.

Cracking permits the formation of new and more volatile hydrocarbons, the majority of which will be condensable at temperatures of 30° C. (86° F.), and upwards. The maintenance of gases resulting from the cracking, such as hydrogen, methane, ethylene, ethane, etc., having boiling points below 30° C, in the cracking zone, has an important influence on the results.

It is well known that in chemical reactions there is a tendency to establish and maintain a state of equilibrium. For example, in the cracking of the gaseous hydrocarbons as above described, two classes of gases are formed, i.e., those condensable at about 30° C, and those uncondensed at this temperature. If the condensable gases be withdrawn or removed, the cracking being continued, the other, or permanent gases, or a very considerable proportion of them being in the sphere of reaction, there will be a tendency to restore the equilibrium and form condensable hydrocarbons rather than those not condensable at temperatures above 30° C. This tendency to form condensable hydrocarbons will be promoted by high concentration or increase of the density of the permanent gases in the sphere of reaction. To this end, a pressure of at least six atmospheres is maintained in the reaction zone. Rittman states that he prefers to obtain the pressure by controlling the discharge of the gases from the reaction zone. Although the best results can be attained by employing for a given material, a certain temperature and a certain pressure, these two are in no way interdependent, although it is generally preferred to use high pressures with high temperatures and these pressures and temperatures are those which cannot generally be obtained in a two phase system. While the pressures employed will vary with the character of the material treated
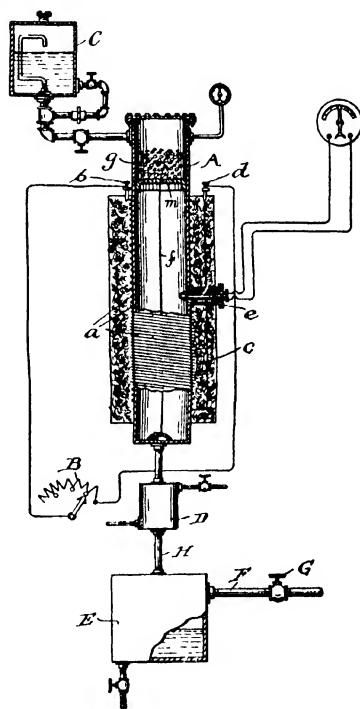
Fig. 137. — Diagram showing principle of the Rittman process.

and the character of the products desired, the best results will be obtained by maintaining a pressure of about 100 pounds and higher in the generating zone, the efficiency of the process increasing as the pressure employed is increased.

In Fig. 137, A is a chamber capable of withstanding the pressure and constitutes the hydrocarbon cracking zone. a is a resistance wire, properly insulated, in contact with A which is incased in a protective coating of asbestos. b and d are binding posts. c is a conducting rod through which one end of the resistance coil is connected to binding post d. B is a rheostat. e is a branch tube opening into A through which the pyrometer couple is introduced. f is a rod to support a perforated disk m which supports a quantity of filling material g introduced into the upper portion of A. This filling material serves as an efficient spreading surface for vaporizing the oil used, as well as a heat conductor and heat disseminator. C is a feed cup for supplying oil to A above g. The pressure in the upper part of C is equalized with that in tube A through an equalizing connection. A may also be connected with a suitable gage for reading the pressure. D is a condenser which leads through a pipe H to a receptacle E for the collection of liquid distillates. F is a pipe and G a release valve through which the gaseous products evolved during the process may be permitted to escape into a gas holder not shown. Condenser D is cooled to a sufficient degree to condense all vapors. Condensate passes through H to a collecting vessel E from which the product may be withdrawn and fractionally distilled.

With the type of apparatus shown, the procedure is as follows: The cracking or reacting chamber is heated to the cracking temperature of the material by passing an electric current through the heating element a. When the tube A and the filling material g have attained the appropriate temperature, the feed is opened and the material is permitted to enter the upper part of the tube A, where it spreads over the filling material and is flashed or instantaneously gasified. In the meantime the valve G has been closed in order to bring the concentration of permanent gases to the desired point. After the desired pressure has been attained valve G can be opened from time to time to release excess pressure created in A. The hydrocarbon gases pass into the cracking zone of the tube A. After passing through the cracking zone, the hydrocarbon gases are condensed and collected in receptacle E, thereby being removed from the sphere of reaction.

In common with other single phase systems either naphtha or benzene, toluene, etc., can be produced from a large variety of raw material.

The following are examples:

A. *Production of benzene-toluene.* Two thousand gallons of gas oil containing no free benzene or toluene were taken. This oil was treated in a heavy steel tube of $10\frac{3}{4}$ inches internal diameter and 13 feet long, under a furnace temperature of approximately 1000° C. (1832° F.), and a pressure of 150 pounds per square inch. Oil was fed to the tube at the rate of about sixty-two gallons per hour, the whole quantity above referred to being converted in approximately thirty-two hours. Five per cent (of the initial quantity) of benzene (benzol) and toluene, namely, ten thousand gallons of each, were recovered by re-running the

distillate.   The Rittman process may also be employed for cracking solvent naphtha with the consequent-production of toluol. * It has been so employed to produce toluol for military purposes.   The process gave yields of toluol varying from 25 to 33 per cent, based on the solvent naphtha employed.

B. *Production of naphtha*   An average of 16,800 gallons (400 barrels) of gas oil were treated daily, from which there were recovered approximately 5000 gallons (119 barrels) of gasoline, with a total over all loss varying from four to six per cent.   This corresponds to a yield of 29.76 per cent of gasoline, based on the gas oil employed.   The number of tubes that are employed depends on the capacity requirements of the plant.

In the present example, a battery of four tubes was used, each tube being ten inches in diameter, twelve feet in length and standing in an upright position.   Each tube was supplied with gas oil (preheated to about 500°F.) at an average rate of about 175 gallons per hour.   The temperature in the tubes varied from 1080° to 1200° F. (582°–649° C.); and the pressure varied from 80 to 100 pounds per square inch, depending on the characteristics of the gas oil used as cracking stock. All the fuel necessary to maintain the requisite heat conditions was furnished by the by-product gas from the cracking tubes.

C. P. Bowie [1] describes the construction and operation of a single tube cracking furnace for making gasoline.   In operating the Rittman vapor phase cracking process, with furnaces containing several tubes, e.g., ten, an even temperature is difficult to maintain and the single tube furnace is preferred.   The tube is of steel and lap welded, 13 to $13\frac{1}{2}$ feet long over all, 13 to 14 inches outside diameter, and with walls about 1 inch thick.   It is connected to a tar pot from which carbon and tar can be easily removed when necessary.   In the inside of the tube, at the top, is a cast steel basket which serves as a bearing for the stirring rod (which occupies the center of the tube and prevents its choking by deposited carbon) and as a receptacle for steel balls or other pieces of metal over which the oil passes before entering the tube. Vaporization is, however, more suitably effected by means of a spray nozzle.   The stirring rod is made from 3 inch extra strong pipe, to which are fastened four vertical rows of chains 3 inches apart.   The rod enters a stuffing box and gland which are placed in the tar pot. On the lower part of the stirring rod is a cast iron paddle, to prevent carbon from accumulating on the stuffing box and choking the neck of the tar pot.   Before entering the tube the oil is strained and heated

[1] J. S. C. I. 1917, 285; U. S. Bureau of Mines, Tech. Paper 161, 1916.

to about 100° C. From the preheater the oil passes through another strainer, a meter, and a needle valve for regulating flow, into the cracking tube. By means of a pressure reducing valve, condensation of the cracked products takes place at practically atmospheric pressure in the ordinary box type of condenser. The cost of the plant, exclusive of a building or other protective covering, and condenser box, is said to be about $3000. After removal of gasoline from the cracked oil by distillation, the residuum may again be cracked but should not be mixed with the original oil, as "once cracked oil" may require different temperatures and pressures for re-cracking, and yield a distillate of a different specific gravity from that of the cracked oil originally obtained.

In operation on the large scale, the cracking tube likewise is provided with an agitator having chains attached, and a tar pot at the bottom. According to Bowie (Construction and Operation of a Single Tube Cracking Furnace for Making Gasoline, J. S. C. I. 1917, 285; U. S. Bureau of Mines, Technical Paper 161, (1916)) this has always been a special casting. The tar pot calls for three essential features: it must be fitted with a stuffing box and a gland for the stirring-rod shaft, it must allow easy removal of carbon and tar, and must be heavy enough to withstand the required pressure. It is said that all of the pots heretofore cast for this purpose have been too elaborate.

The following U. S. Government estimates[1] are based on the results of a 5-days run with a Rittmann apparatus provided with five cracking tubes, each having a capacity of about 65 gallons per hour; allowing for stoppages, the total working capacity is 5000 barrels (42 gals. each) per month. The yield of gasoline is about 17 per cent and the loss 10 per cent, while the residue consists of fuel oil equal in value to the fuel oil used as raw material. The cost of the plant is estimated as $15,000, and of the building as $5000. Using fuel oil at 50 cents per barrel, the cost of production of gasoline is estimated as follows:

5000 barrels fuel oil...	$2500
Labor.........	560
Fuel..	160
Electricity	100
Repairs	100
Interest and depreciation, 6 % each	200
Refining cost, 20 cents per barrel .	1000
Total cost	$4620
Residue, 3650 barrels at 50 cents per barrel	1825
Net cost of 850 barrels of gasoline	$2795

Corresponding to 7.8 cents per gallon of gasoline.

In a similar way, the cost of gasoline is estimated as 9.74 cents per gallon with fuel oil at $1 per barrel, 11.5 cents per gallon with fuel oil at $1.47 per barrel, and 13.9 cents per gallon with fuel oil at $2.10 per barrel.

[1] Min. and Eng. World, 1916, 1132; J. S. C. I. 1916, 825.

In carbureting water gas Rittman departs from the ordinary carbureting procedure.[1] In place of the ordinary carbureting chamber a cracking tube is situated therein heated by the hot blast gases.   Oil gas is fed to this tube and is cracked in the vapor phase at a temperature of approximately 1600° F. (871° C.) and under a certain amount of reduced pressure, for example 4 pounds absolute or less.   It is stated that the gases produced under these conditions of temperature and pressure are largely of the ethylene and other unsaturated series and
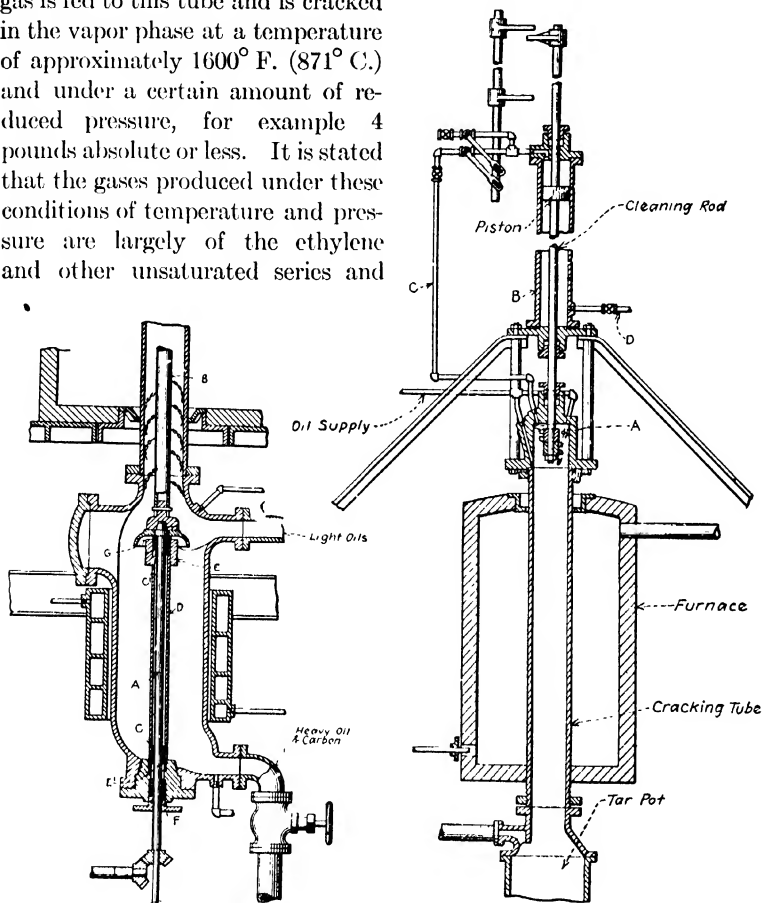
Figs. 138 and 139. — Types of tar pots and stirring rods devised by Slocum and Stutz for the Rittman process.

are therefore much higher in thermal values and illuminating qualities than gases produced by the ordinary carbureting method. Hydrocarbon gases produced in the manner indicated are mixed with water gas to " enrich " the latter.

[1] U. S. Patent 1,329,853, Feb. 3, 1920.

F. L. Slocum and **C. C. Stutz**[1] have designed improvements in the stirring rod connections and tar pot for use in the Rittman process, as shown in Fig. 138. The stirring rod does not itself pass through a stuffing box in the bottom of the tar pot as in older types of the apparatus. The stirring rod B is attached to a driving shaft A (which is provided with bearings C and C') and this shaft is incased by a stationary tube D. This tube D engages a supporting collar E, at its upper end, and a female thread E' at its lower. An ordinary stuffing box and gland F are provided on the outside of the tar pot. An umbrella-shaped casting G tends to prevent carbon from clinging to the surface of D. In this method, heavy oils are pumped back to the tar pot and used to wash the latter free from carbon deposit.

Slocum and **Stutz**[2] have also designed a stirring, or rather cleaning rod (Fig. 139) which has an up-and-down, instead of a rotatory movement. Scrapers on the end of this rod are intended to remove carbon deposit from the walls of the cracking tube. The cleaning rod is automatically actuated by oil vapor pressure from the cracking tube which exerts force on the upper side of the piston on the completion of its upward stroke, by admission of pressure through the pipe C, and on the lower side of the piston, at the completion of its downward stroke by admission of pressure (from the cracking tube) through the pipe D. Pressure developed in the cracking tube is thus caused to do mechanical work.

It is pointed out by Rittman[3] that in most cracking processes the heat of the hot vapors as they leave the cracking apparatus is wasted during the passage of the vapors through condensing apparatus. It is suggested that as much as possible of the heat in the condensate be utilized by applying a vacuum to enable lighter hydrocarbons to boil off. Uncondensed gases are scrubbed to recover light gasoline.

[1] U. S. Patent 1,304,211, May 20, 1919.
[2] U. S. Patent 1,304,212, May 20, 1919.
[3] U. S. Patent 1,330,008, Feb. 3, 1920.

CHAPTER XVI

THE USE OF STEAM IN DECOMPOSING HEAVY OILS TO YIELD NAPHTHA AND GASOLINE

The reaction between steam and metals to produce energized or "nascent" hydrogen is the basis of a large number of methods, whose object is to try to bring about a reaction between hydrogen and hydrocarbons that are in a state of transition. In a purely numerical sense, the addition of hydrogen to saturated high boiling oils, undergoing decomposition, will produce ratios of carbon and hydrogen which are identical with those of low boiling oils of the same series. For example,

$$C_{12}H_{26} + 2 H = 2 C_6H_{14}.$$

This is merely another way of stating that when a saturated straight chain hydrocarbon of higher molecular weight is decomposed to yield one of lower molecular weight, the result must be the production of an unsaturated straight chain hydrocarbon, or saturated cyclic hydrocarbon *unless* some other modifying chemical reaction takes place. One of the basic reasons for the existence of the large variety of cracking processes is the opportunity offered for the application of different methods of effecting the modifying, or secondary reaction mentioned above.

Compression of the "wet" gases with the unsaturated readily condensable hydrocarbons, condensation under pressure, the aluminum chloride reaction, decomposing in the presence of hydrogen, or hydrogen-containing gases in the presence or in the absence of energizing, concentrating or accelerating conditions — e.g., silent electric discharge, ultraviolet light and catalytic masses - these are types of methods proposed for bringing about the decomposition of high-boiling oils into a mixture of low-boiling hydrocarbons which shall have a suitably low "unsaturated" value, in a manner calculated to yield minimum percentages of gas and precipitated carbon or carbonaceous material.

In this chapter we will consider those methods that involve decomposition in the presence of steam. This includes methods whose object is to decompose the steam in such a manner as to yield hydrogen. Some of the catalysts proposed are intended to accelerate this decomposition at relatively low temperatures.

Sanders [1] made illuminating gas by passing a mixture of oil, or oil vapor, and water vapor into contact with red hot carbon. Coal tar oils were preferred as raw material.
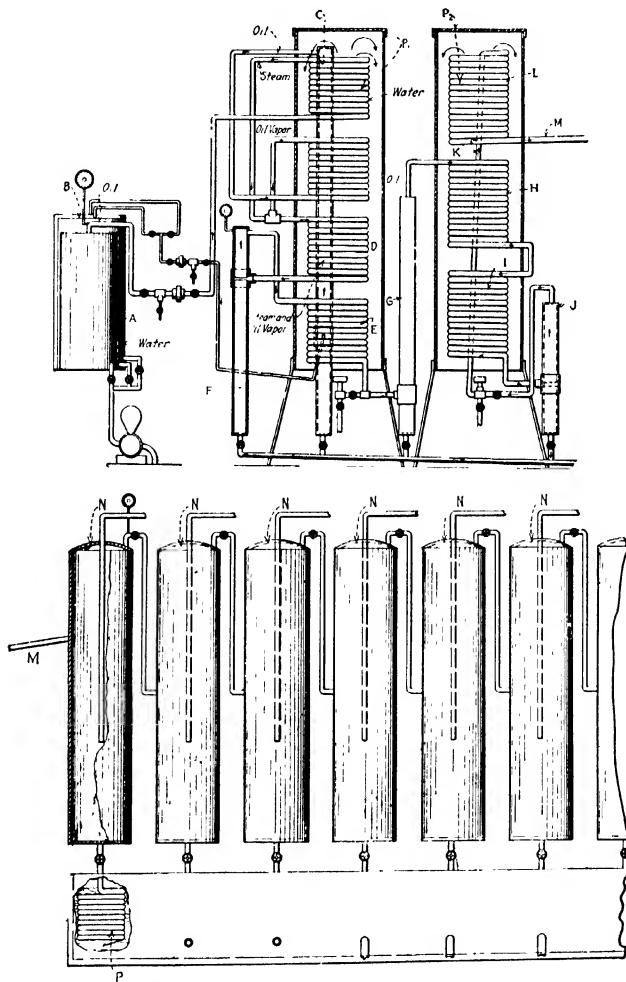
Figs. 140 and 141. — Apparatus proposed by C. W. Turner.

John Laing [2] mixed oil and water and passed the mixture through retorts heated by the hot gases from the combustion zone of a fire tube

[1] U. S. Patent 21,027, July 27, 1858; Reissue No. 936, March 27, 1860.
[2] U. S. Patent 31,985, April 9, 1861.

boiler. The object was to utilize excess heat to generate oil gas and thus make the operation of raising steam " self-supporting."

Eames and **Eames** [1] describe an apparatus for making oil-gas in which oil flows in a zig zag path over highly heated plates in the presence of superheated steam.

C. W. Turner [2] thoroughly mixes crude petroleum or a distillate with superheated steam and passes the mixture through two series of coils of pipe (Fig. 140), P_1 and P_2. The first series (P_1) is heated from 400° to 800° F. (204°–427° C.). Here it is said that a reaction takes place between the superheated steam and a portion of the oil vapors, with the production of carbon monoxide and nascent hydrogen. The hydrogen, it is stated, combines with unsaturated hydrocarbons. The pressure in the first series of coils is about sixty pounds per square inch. The pipe of which the coils are constructed is 2 inches in diameter.

A preheating drum C (Fig. 140) and also separating drums F, G, and J are employed to remove mineral matter and tarry substances. The temperature in the second series of coils (P_2, Fig. 140) is carried up to 1000° to 1400° F. (538°–760° C.). This is said to cause, in some cases, the formation of naphthalene, which is precipitated in the separator J. The distillate is fractionally condensed in a series of air-cooled tanks (N, N, N, etc. Fig. 141) provided as shown at P (Fig. 141) with cooled drain or draw-off pipes. [3]

A. B. Adams [4] cracks oils for the production of low-boiling hydrocarbons and gas, by mixing them with steam, passing the mixture through a cracking chamber, and then, at the exit of the cracking chamber, bringing the products into contact with a finely attenuated mass of catalytic metal.

H. H. Mandle [5] obtains gasoline, benzol, toluol, etc., from heavy oil by mixing the heavy oil with water, spraying the mixture into a heating chamber or tubes heated to a temperature of from 250° to 675° C. (482°–1247° F.) and subjecting the mixture to the action of a catalytic agent consisting of an alloy of nickel, chromium and steel placed at the outlet end of the chamber or tubes, the mixture being then passed through an oil-cooled primary condenser for removing the uncracked oils and a water-cooled secondary condenser for condensing the hydrocarbons of lower boiling point. The alloy may be in the

[1] U. S. Patent 132,265, October 15, 1872.

[2] U. S. Patent 1,046,683, Dec. 10, 1912.

[3] See also Turner, Chem. Abs. 1913, 3225; French Patent 451,162, Nov. 28, 1912.

[4] Chem. Abs. 1919, 184; British Patent 119,485, July 5, 1917.

[5] Chem. Abs. 1919, 184; British Patent 119,284, Sept. 27, 1917.

form of woven wire or may be included in the composition of the walls of the cracking tubes; or a stirrer or scraper may be made of the alloy. The pressure in the heating chamber or tubes may vary from atmospheric to 600 pounds per square inch.

J. Oltmans[1] converts higher hydrocarbons into lower hydrocarbons, e.g., coal tar or tar oil to benzol, petroleum to benzine, etc., by vaporizing the oil and mixing the vapor with steam at 5–6 atmospheres, thorough admixture being insured by passing the mixed vapors through a zig zag length of piping. The vapors then pass through a mass of coal or coke previously brought to incandescence by ignition in a current of air. The products of reaction pass through a scrubber, and are then mixed with a further quantity of steam and pass into a condenser. The aqueous portion of the condensed liquid is separated and the remainder purified by distillation.

In the manufacture of a combustible liquid according to **N. Falk-Hultgren** and **E. H. Vidstrand**[2] compounds of the methane, ethylene, or benzene series, such as the dry distillation products from peat, coal, etc., are heated with water vapor to 2000° C. (3632° F.). The resulting liquid consists of a mixture of several heavy hydrocarbons and their isomers, and in composition is said to be intermediate between the methane and the ethylene series.

Gasoline practically free from unsaturated hydrocarbons is claimed to be obtained by **E. L. Davies**[3] from a high-boiling petroleum oil by mixing the vaporized oil with superheated steam and passing the mixture under pressure through a tubular cracking apparatus packed with iron or steel shavings. The yield of gasoline is reported to increase with the pressure, up to 100 pounds per square inch, which was the highest pressure employed, and the best results were obtained by using about 10 pounds of steam per gallon of oil, superheating the steam to at least 600° C. (1112° F.) and cracking at 650° to 675° C. (1202°–1247° F.). The loss of oil through carbonization, gas formation, etc., was 10–12 per cent and the iron or steel shavings had to be frequently renewed. The gasoline obtained resembled commercial 72° Baumé · naphtha (specific gravity 0.693) in its properties and its behavior when used in motor cycle and automobile motors. The cost of production in cents per gallon is estimated to be one and one-third times the cost of the oil used as raw material plus ninety per cent.

[1] J. S. C. I. 1918, 295A; British Patent 108,454, Jan. 2, 1917; Int. Conv., Aug. 1, 1916.

[2] Chem. Abs. 1915, 2452, 148; Norwegian Patent 24,576, Jan. 18, 1913.

[3] J. S. C. I. 1916, 461; J. Ind. Eng. Chem. 1916, 114–118.

Shedlock and the **Optime Motor Spirit Syndicate** [1] emulsify the cracking stock with water by means of an emulsifying agent (for example, resin soap) and then force this mixture through a retort under pressure (3 to 6 atmospheres) which is packed with iron, steel, or nickel shavings and heated from 500° to 900° F. (260°–482° C.). Nascent hydrogen is said to be produced by the action of the steam on the metal. The reaction products are expanded and dephlegmated, light oils recovered and heavier oils sent back to the supply vessel.

R. H. Brownlee [2] increases the yield of low boiling liquid products by introducing steam into the lower extremity of a vertically extending pipe system maintained at a temperature of over 800° F. (427° C.) and a pressure of over five atmospheres. Oil is injected below the upper extremity of the system, and a reflux of heavy oils takes place so that heavier components separating at any point undergo a further treatment in the presence of a smaller concentration of the lighter products than at the point of their separation.

Moeller and **Woltereck** [3] pass the vapors of heavy oil mixed with highly superheated steam through iron tubes heated to 600° to 800° C. (1112 1172° F.). The tubes are filled with broken coke and it is said that nascent hydrogen is produced by the reaction between the coke and superheated steam. It is also said that this nascent hydrogen aids in breaking down molecules of higher into those of lower molecular weight, and that this produces an increased yield of light hydrocarbons. No superatmospheric pressure is used. The steam is superheated to 700° to 800° C. (1292°–1472° F.) in an apparatus which allows the steam to expand while it is being heated.

Schiller [4] boils crude petroleum containing sulphur, or distillates, with the addition of zinc dust and dry caustic soda. Two effects are said to be obtained: (1) the conversion of organic sulphur into hydrogen sulphide and ultimately to zinc sulphide and (2) the decomposition of the higher boiling oils into burning oils. It is set forth that the nascent hydrogen evolved aids this decomposition.

T. G. Hall [5] subjects crude oil containing sulphur to low cracking temperatures in the presence of steam and large surfaces of refractory materials and finds that besides removing sulphur from the oil the Baumé gravity of the latter is increased, i.e., cracking takes place.

[1] British Patent 1878, Jan. 23, 1914.
[2] Chem. Abs. 1919, 185; Canadian Patent 185,052, June 25, 1918; U. S. Patent 1,320,376, Nov. 4, 1919.
[3] British Patent 16,611, July 19, 1913.
[4] U. S. Patent 580,652, April 13, 1897.
[5] U. S. Patent 372,672, Nov. 8, 1887.

The converter has a diameter of about ten feet and a length of about thi.t· feet, and is filled a little more than half-full with fragments of granite about two or three inches in diameter. Into the bottom of this still, through a suitable perforated pipe or pipes, extending the length of the still, the crude oil and steam are injected, using a steam injector. The still itself is constructed so that a high temperature can be obtained, especially in the upper part of the granite. This temperature ranges from 420° to 460° F. (216°–238° C.) though higher temperatures are used under some conditions. In the presence of highly-heated blocks of granite at these temperatures it is stated that the sulphur leaves the oil, and in the condition of sulphureted hydrogen passes into the water, where it is detected by the usual tests. As a result of this treatment it was found that the specific gravity of the oil had been diminished, or its degree, Baumé, increased. Taking a 32° gravity Canadian oil, the gravity of the first run was found to be from 47 to 48° on an average. This oil, the gravity of which had been increased from about 32 to 48° Baumé was rerun through the same converter and condenser as before, with an additional supply of steam. The result of this second treatment was to
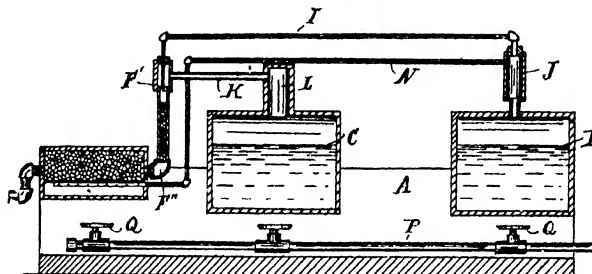
Figs. 142. — Hawes' apparatus employing gravel as contact agent.

still further purify it. The average gravity was likewise somewhat increased in this second run, generally from one to two degrees. Marble, quicklime, and cryolite were also found to give satisfactory results.

B. N. Hawes [1] passes a mixture of steam and oil vapors through a mass of gravel heated to 400° to 600° F. (204°–316° C.) in order to desulphurize the oil. A certain amount of cracking is also said to take place.

The apparatus used is shown in Figs. 142 and 143.

Chamber D, Figs. 142 and 143, is connected with a vertical cylindrical chamber F' by means of a coupling F''', above which is arranged a perforated diaphragm G, for supporting a filling of gravel G', the chamber being filled to about one-half its height, leaving a space above the gravel, into which is inserted the end H of a pipe I, leading from a dome J in the boiler B, the end H extending sufficiently into the chamber F' to cause a vacuum in it when sufficient steam is injected into F' to siphon the vaporized hydrocarbon oil contained in the vaporizer C, there being a pipe K leading from a dome L in the vaporizer, and tapped into the upper end of chamber F'.

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[1] U. S. Patent 444,833, Jan 20, 1891.

Chamber D has a perforated diaphragm D', extending longitudinally, upon which rests a filling of gravel M, entirely filling the remaining upper portion of the vaporizer. N is a pipe tapped into the dome J of the boiler and provided with a perforated end portion O, which extends into the desulphurizing-chamber below the diaphragm for the purpose of delivering a series of jets of steam. P is a pipe for conveying either a gaseous or liquid fuel to burner Q, located beneath the boiler vaporizer and desulphurizing-chamber for generating steam in the boiler, vaporizing the oil in the vaporizing-chamber, and heating the combined vapor sufficiently to release the sulphur, which unites with and is carried off with the water of condensation. It is stated that to insure union of the hydrogen and sulphur there must be an intimate mixture of the steam and hydrocarbon vapor in a proper proportion prior to the release of the sulphur. To insure this intimate mixture the vapors are first passed through the gravel in chamber F', where the agitation caused by the jet of steam forcing the intermingled vapors rapidly through the gravel "atomizes" the vapors. They are then passed into the desulphurizing-chamber D, where the commingled vapors are heated to a temperature sufficiently high to cause the sulphur to separate from the oil vapor and combine with the hydrogen, this temperature being from 400° to 600° F. (204°–316° C.), throughout the

Fig. 143. — Detail of Hawes' apparatus showing gravel packing.

entire interior surface of the chamber. To prevent discoloration or injury to the hydrocarbon vapor while being subjected to the intense heat necessary to insure disintegration there is a series of jets of steam impinging upon and rising through the gravel from the perforated end O of pipe N, which in the process of superheating from the normal temperature of from 212° to 250° F. (100°–121° C.) supposedly assists in bleaching and deodorizing the oil vapors

The water of condensation is said to be of a black or inky color of sulphurous odor, leaving the distillate bleached, deodorized, and of a high grade fire test.

Mengel and **Von Pöhrnhoff** [1] reported obtaining a larger yield of illuminating oil from petroleum residuums by dropping liquid water on to highly heated residuums contained in a still.

They state that in the ordinary process of distilling petroleum to obtain illuminating oil there is always a tarry residuum, from which no more oil suitable for illumination can be obtained and that attempts made to effect the distillation or conversion of illuminating oils from this residuum by the introduction of steam into the still were without success. It is stated that by the introduction of water in a liquid state into the still, and in contact with the residuum, while the latter is heated to the high temperature of from 600° to 800° F. (316°–427° C.), a very large proportion, namely, from eighty-five to ninety per cent, of the tar oil may be converted into illuminating oil. The still, in its head or upper part, is furnished

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[1] U. S. Patent, 116,852, July 11, 1871.

with a cock, above which is a funnel, with a siphon-trap between it and the cock. The funnel is kept supplied with water. When the residuum in the still has been heated to above 600° F. (316° C.) the cock is opened and water allowed to drop into the still and fall upon the surface of the tar or residuum. The vapors thus eliminated pass out of the still, and are condensed in the usual way and collected in the form of illuminating oil, which, though of dark color, is of a light specific gravity.

It is stated that from petroleum residuum of a gravity of 25° Baumé, about eighty-seven per cent of dark oil was obtained, all of which was consumed in a lamp, and which burned freely to the last drop. The quantity of water dropped
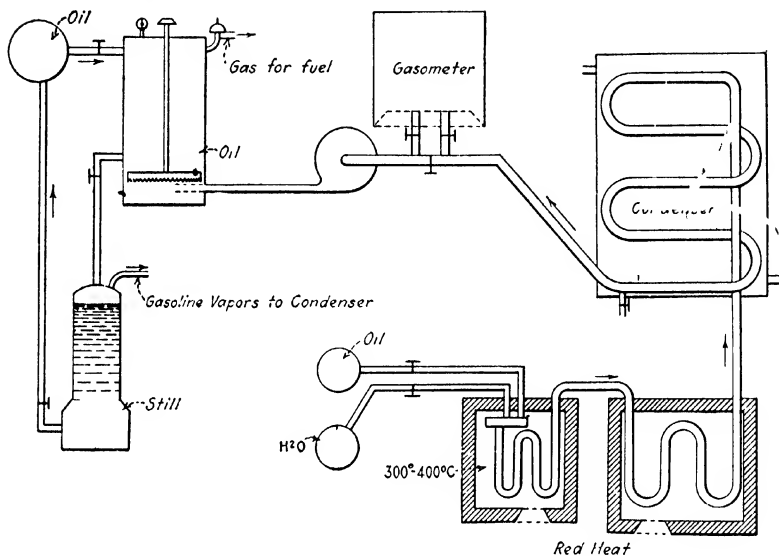
Fig. 144. — Zerning's tube-cracking apparatus.

into the still is regulated by opening the cock more or less, and depends upon the quality of the residuum to be converted and the temperature of the still. Generally during the process a quantity of water about equal to from one to three per cent of the tar or oil is used.

H. Zerning[1] prepares reactive products from hydrocarbons by spraying paraffin oils and water into a system of tubes, of which the first section is heated to about 300° C. (572° F.) the next to above 500° C. (932° F.) and the last to about 700° C. (1292° F.), the most favorable excess pressure being 0.2 atmosphere. Highly reactive products are obtained, which can be readily oxidized, nitrated and sulphonated. For example, the product from high-boiling American petroleum yields with sulphuric acid, bodies resembling shellac, with

[1] J. S. C. I. 1917, 541; German Patent 295,594, May 5, 1915.

nitric acid and potassium permanganate oils with a pleasant odor, and by simple nitration, products which can be used in the manufacture of explosives.

Zerning [1] treats a variety of organic liquids by saturating them with gases and vapors and then distilling. It is maintained that the result of the method is the conversion of substances of high boiling point into more volatile bodies. The liquids which are saturated are: (a) mineral oils, (b) mixtures of animal and vegetable oils with fats and hydrocarbons or alcohols, (c) mixtures of hydrocarbons and alcohols.

For obtaining light hydrocarbon gases to be used in impregnating heavier oils, Zerning [2] passes a mixture of about one part water and 6 to 10 parts of petroleum oil through pipes coated with fire clay which are heated to 300° to 400° C. (572°–752° F.). The resulting mixture of steam and hydrocarbons is then passed through tubes heated to a dark red heat. By leading the resulting hydrocarbon gases into oil of specific gravity 0.794 under slight pressure, the specific gravity of the oil is lowered to 0.775 and the flash point lowered to 10° C. (50° F.). Figure 144 shows the apparatus used for this work.[3]

C. H. Washburn [4] transforms kerosene and petroleum products of 26° to 48° Bé. (specific gravity 0.901 0.901) into a product of Baumé gravity not exceeding 52° (specific gravity 0.777) by heating with water in a retort at 650° to 950° F. (340°–510° C.), and condensing the vapors under a pressure of 3 to 5 atmospheres which is maintained both within the retort and the condenser.

According to the **New Oil Refining Process, Ltd.,**[5] in cracking mineral oils, 3 parts of the latter are conducted, in liquid or vapor form, together with water, 1 part, into a refractory retort, free from air and heated to 540° to 650° C. (1004°–1202° F.) which is filled with copper, aluminium, alumina, bauxite, iron carbide, or their mixtures.

O. B. Evans [6] states that when coal tar heavy naphtha is decomposed or " fixed " in the presence of steam or water gas, less lamp black is formed than when this decomposition takes place without such an admixture of steam or water gas.

V. Meunier [7] uses a mixture of steam and oil vapors at high pressure (14 atmospheres) and temperature 1400° F. (760° C.) in order to

[1] J. S. C. I. 1913, 781; French Patent 452,919, Jan. 6, 1913; Int. Conv. Dec. 13, 1912, and first addition thereto of Jan. 14, 1913; Int. Conv. Jan. 6, 1913.
[2] British Patent 731, Jan. 9, 1913.
[3] See also Zerning, U. S. Patent 1,183,266, May 16, 1916.
[4] J. S C I. 1915, 651; U. S. Patent 1,138,266, May 4, 1915.
[5] Chem. Abs 1913, 3225; French Patent 451,471, Dec. 5, 1912.
[6] U. S. Patent 1,230,087, June 12, 1917.
[7] U. S. Patent 1,053,074, Feb. 11, 1913.

produce a maximum volume of high candle power oil gas. Checker brick work forms the construction of the converter.

Dibdin and **Woltereck** [1] decompose crude petroleum in the presence of highly heated iron, or iron oxide, using steam to furnish hydrogen by the action of the metal. The temperatures used are bright red to orange and the pressure is only very slightly superatmospheric, since the object in view is the production of a maximum volume of permanent gases, consisting chiefly of hydrogen, methane and carbon monoxide.
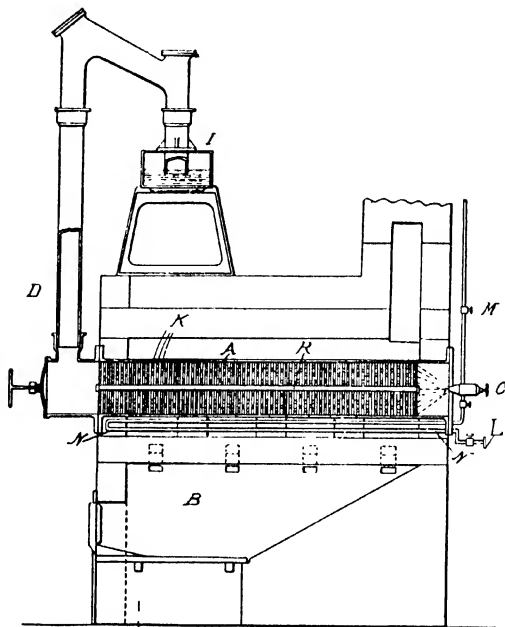
Fig. 145. — Apparatus of Dibdin and Woltereck for decomposing oil in the presence of steam and heated iron.

The process is based on the decomposition of steam by iron at high temperatures producing hydrogen and metallic oxide. A portion of this oxide reacts with the hydrocarbon compounds in the oil, forming water and carbon monoxide, which reduces the remaining oxide back to the metallic state, with the production of carbonic acid. The following equations illustrate the reactions assumed to take place in the process of oxidation and reduction of the metal. Taking M as the symbol of the metal and C_nH_{2n-2} as that of the hydrocarbons, we have —

$$\text{I.} \quad 2nM + 3nH_2O = nM_2O_3 + 6nH$$
$$\text{II.} \quad nM_2O_3 + C_nH_{2n-2} = 2nMO + nCO + (2n-2)H.$$
$$\text{III.} \quad 2nMO + nCO + 2nH = 2nM + nCO_2 + nH_2O.$$
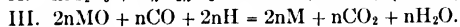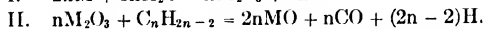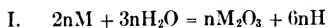
[1] British Patent 19,152, Sept. 25, 1901.

r resuming these three reactions in one:

$$2nM + 2nH_2O + C_nH_{2n-2} = 2nM + nCO_2 + (6n - 2)H$$
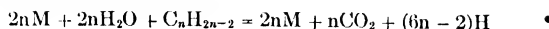
The metal acts as a carrier of the oxygen from the water to the carbon of the hydrocarbon. In case it is found desirable the contact material may be composed partly or totally of the oxide of a suitable metal. In this case reactions II and III occur primarily in place of reaction I.

The excess of hydrocarbons present is during this process broken up into less complex molecules, or reacts with the hydrogen to form new compounds producing methane, ethylene, etc., which furnish the illuminating power to the gas produced. By varying the proportions of oil and steam according to the desired illuminating power, the quality of the gas may be varied. With the minimum of oil required for the process of reduction, a production of about 200,000 cu. ft. may be obtained of a gas of low illuminating power but ideal quality as power gas in not containing any incombustible gases after purification (practically all carbonic acid being removed), and consisting chiefly of hydrogen, methane and carbon monoxide. The metal is employed in the form of perforated disks, which may be strung on a central rod to enable them to be easily removed for inspection and which should fit into the retort employed as closely as possible.

In Fig. 145, A is the reaction chamber formed by an iron retort, built into the regenerator furnace B. A is filled with the contact material in the form of perforated iron disks K, strung on the central rod R. The retort is provided with the injector C for the introduction of oil and steam which are supplied to it by pipe M for the oil and pipe L for steam which is superheated in the coils NN placed in the furnace below the retort A. The gas formed escapes through D and the hydraulic I to the condensers and purifiers as usual in gas works.

Dibdin and Woltereck [1] commenting on the use of steam in producing oil gas, state that the production of a maximum volume of high candle power gas is hampered by the formation of considerable fixed carbon. It is noted that the production of relatively small volumes of gas of good candle power is not difficult but that if it is attempted to use very high temperatures (white heat) in order to increase this volume, then the illuminating power falls off with the simultaneous increase in production of fixed carbon. It is stated that this difficulty may be very considerably helped by passing oil vapors and steam through retorts packed with a mixture of ferrous and ferric oxides at a bright orange heat. The catalyst is made by packing the retorts with iron tubes, heating to a bright red heat and then passing a mixture of oil-vapors and steam through the retorts at this temperature for several days. This converts the iron into mixed oxides. Some free ferrous oxide should be present.

W. A. Hall [1] reports making an oil gas (containing the substances

[1] British Patent, 26,666, Dec. 21, 1905.

[2] U. S. Patent 1,105,772, Aug. 4, 1914.

listed below in the proportions named), by forcing a mixture of water and heavy oil through a mass of catalytic nickel.

Methane	48.6%
Ethylene	40.5
Hydrogen	6.4
Nitrogen	1.79
Oxygen	1.10
CO and CO_2	1.6
H_2S and CS_2	none

It is to be noted that Hall states that the temperatures employed (650° to 750° C. i.e. 1202°–1382° F.) are above "that at which the catalytic properties of nickel are destroyed by union with sulphur, that, on the contrary, sulphur (under the conditions used) would be converted principally into the form of hydrogen sulphide."

A mixture of oil and water, in equal proportions, is passed thro...........ed receptacle containing metallic nickel, which may be in the form of shot, or small irregularly shaped pieces, and which is maintained at a temperature high enough so that the nickel will cause the dissociation of water into its elements, which temperature is also high enough so that nickel oxide cannot exist in the presence of the reducing agents present, such a temperature being, for example, about 650° to 750° C. (1202°–1382° F.). Under these conditions the hydrocarbons of the oil are first cracked into hydrocarbons having a smaller number of carbon atoms, and a part of the water present is converted into hydrogen and oxygen. The hydrogen attaches itself, it is said, to some of the unsaturated hydrocarbon bodies present, and the oxygen attaches itself to carbon atoms, forming principally carbon monoxide, although there may be some carbon dioxide also produced, since it is practically impossible to maintain the temperature exactly at the point at which carbon monoxide will be formed exclusively instead of some carbon dioxide. In carrying out this process crude petroleum oil may be employed, although for economical reasons, it is preferred to use "still bottoms" or "stripped oil," or oil from which at least the gasoline and kerosene fractions have been distilled. Should the oil employed contain material quantities of sulphur, such as Beaumont oil, Lima oil, or certain of the Canadian oils, which are high in sulphur, this sulphur would not materially injure the nickel, since the temperature is above that at which the catalytic properties of nickel are destroyed by union with sulphur, but on the contrary this sulphur would be converted principally into the form of hydrogen sulphide although small amounts of carbon disulphide might be formed. These sulphur compounds can be removed from the gas by any of the usual methods, if their presence in the gas would be objectionable in the particular process in which the gas is to be employed. In place of pure nickel, nickel containing small quantities of other metals may be used such as cobalt or copper which is commonly associated with nickel; and nickel containing small quantities of cobalt appears to facilitate this reaction, even better than pure nickel.

Owing to the fact that heating the mixture of oil and water to the temperature stated gives some pressure, it is necessary to use a force pump in forcing the oil and water into the decomposing vessel. At this pressure and high temperature,

·there is quite a tendency for the oil in cracking to form a crust or scale on the walls of the decomposing vessel, and on the nickel, but the excess of water always present overcomes this, it is stated, to a large degree. This is one of the reasons why it is necessary to use an excess of water.

Van Steenbergh[1] observes when oil is mixed with superheated steam and subjected to contact with carbon at about 1800° F. (982° C.) that the steam is decomposed, resulting in the production of methane, hydrogen and carbon monoxide, whereas at about 800° to 850° F. (427°–454° C.), the steam is not decomposed and the oil is broken up yielding olefins.

Vernon Boys[2] subjects heavy oil and steam to a temperature of about 315° C. (599° F.).

A. E. Alexander[3] describes an oil cracking apparatus in which steam is said to be decomposed into its elements in the presence of platinum, palladium or nickel at temperatures ranging from about 595° to 875° C. (1100° -1600° F.) and pressures from 250 pounds per square inch down to a minimum pressure.

Within a furnace are three superimposed coils of piping. Water is forced through the top coil, and the steam generated is passed into the bottom of a closed tank containing hydrocarbon oil, thereby forming an emulsion of oil and steam which is forced by air pressure upwards through the middle or "subgenerator" coil on leaving which it passes down a pipe outside the furnace, through an atomizer, and into the upper end of the lowest or "generator" coil. At the lower, outlet end of this coil there is a metallic catalyst (platinum, palladium, or nickel) in the form of a spirally wound coil of wire gradually decreasing in diameter until it merges into a point directed reversely to the flow of the gases. By the action of the catalyst the water vapor is said to be decomposed and the hydrogen formed, together with free hydrogen produced by decomposition of the oil, is caused to combine with hydrocarbons, forming compounds of low boiling point. The apparatus also includes a condenser, a separator, and a scrubber. When it is desired to produce a maximum of fixed gas, the generator is heated to about 1600° F. (about 875° C.) and the pressure is reduced to a minimum; when a maximum of hydrocarbon compounds of low boiling point is required, the pressure is increased to about 250 pounds per square inch and the temperature reduced to about 1100° F. (about 595° C.)

R. B. Day[4] preheats oil and water and pumps a mixture of the two into the upper end of a cracking tube provided with a number of coils situated in a chamber heated from 600° F. (about 320° C.) to 2000° F. (about 1100° C.). At the lower and hotter end of the tube there is a catalyst of nickel-chromium steel in the form of a woven net. The cracked vapors are led off through two condensers, in the first of which

[1] U. S. Patent 1,124,364, Jan. 12, 1915.
[2] Met. and Chem. Eng. 1914, 180.
[3] J. S. C. I. 1918, 683A; British Patent 119,485, July 5, 1917.
[4] J. S. C. I. 1918, 761A.; British Patent 120,230, Sept. 27, 1917.

the cooling medium is the oil under treatment, which is thus preheated, while in the second, water is used. The cracking tubes are arranged in a battery of six, each being supplied by means of a separate pump. An air pump is also connected with the top of each tube in order to blow out the tube when necessary and remove deposits of carbon. A temperature of 1100° F. (about 595° C.) and a pressure of 150 lb. per square inch in the cracking tubes are stated to give good results (in producing motor fuel).

Briefly stated, the process of **C. H. Warth** [1] involves heating a mixture of kerosene and superheated steam to disintegrate the oil. The vapors are passed through an expansion tank, then a condenser; condensed
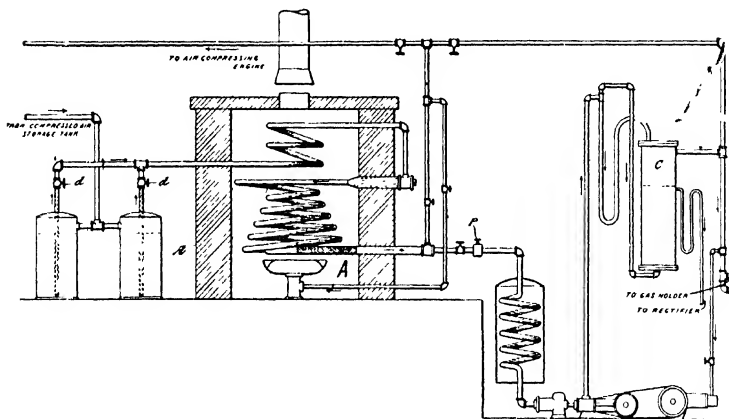
Fig. 146. — Wade's apparatus using nickel.

steam is withdrawn and oil recovered and distilled. The heavier oils are passed through the furnace again.

W. M. McComb [2] mixes hydrocarbons with steam and passes the mixture through a coil of pipe which has a downward pitch or slope, the slope of the pipe increasing as it approaches the source of heat. One of the objects of the process is to give the mixture of vapors a circulatory or gyratory movement so as to aid in obtaining a uniform exposure of all parts of the vapors to the heat applied.

A. B. Adams [3] decomposes hydrocarbon oils by treatment with steam and subsequent cracking. The oil is agitated, emulsified, and "expanded" by means of steam, and the resulting emulsion is treated

[1] Chem. Abs. 1919, 1924; Canadian Patent 191,449, July 8, 1919.
[2] U. S. Patent 1,337,144, Apr. 13, 1920.
[3] Chem. Abs. 1919, 1924; French Patent 486,312, Mar. 22, 1918.

in a generator, where cracking occurs. The resulting gaseous hydro-
carbons and steam are then passed into contact with a finely divided
catalyzer of nickel, platinum or palladium.

Interest may be directed to the process of **H. C. Wade.**[1] This process
deals with passing a mixture of water and oil first through a preheater
and then through a coil of pipe heated to a high temperature. Figure 146
shows the preheating coil arranged above the cracking coil in a furnace
setting. The two tanks on the left contain water and oil respectively.
The portion of the cracking coil marked A in Fig. 146 contains a mass
of catalytic metal, for example nickel. The cracking is conducted
under pressure, and it is said that a formation of naphthenes takes
place previous to the point where the nickel catalyzer is located, and
that when the naphthenes come in contact with the nickel they are
dehydrogenated and yield benzol and toluol.

[1] U. S. Patent 1,336,450, April 13, 1920.

CHAPTER XVII

PROCESSES USING STEAM — *Continued*

Greenstreet Process

The Greenstreet process [1] involves continuously pumping petroleum into flat coils of long pipes with " U " bends under heat, pressure and in the presence of steam. Under such conditions the petroleum breaks down yielding gasoline, making it possible, it is said, to obtain a re- covery of 50 per cent to 60 per cent of volume furnace charge from most of the petroleums of a paraffin base, or a mixed paraffin and asphaltum base produced in the United States. The manufacturing cost, depending upon local labor and fuel conditions, is stated to be approximately 1 cent to 2 cents per gallon for the finished product. The apparatus consists of a furnace in which there are placed six or more long flat coils of 2-inch tubing, each coil having a continuous length of about 425 feet. They are known as cracking coils and are suspended in the furnace from steel beams. These coils have but two exterior connections and are readily removed or replaced within a short period of time by the use of chain lifting blocks.

In the same furnace there is placed another coil of 2-inch pipe, into which the oil is first pumped, which last mentioned coil is not heated to the high temperature of the cracking coils and serves as a preheater. As oil passes from the preheater and just as it enters the cracking coils it is mixed with live steam. Steam and oil vapors enter the cracking coils together and immediately pass into the area of high temperature. This mixture of oil and steam is forced through the cracking coils with great rapidity and the vapors pass into an expansion tank, one of which serves each cracking coil in the furnace. These tanks have the double purpose of equalizing the pressure on the cracking coils and of con- tinuing the cracking of the oil while it is sufficiently hot. From the expansion tanks the oil passes into a condenser coil, and the liquid thus produced is treated in the usual manner for making gasoline. The entire apparatus, cracking coils, preheaters and all the tanks up to the point where the vapors enter the condenser coils, is maintained under high pressure which varies according to the petroleum treated.

[1] R. H. Kinnear, Petroleum Age, 1919 [6], 76–78.

In the construction of the furnace the equipment is entirely supported upon steel framework, with brick enclosures. The firing is accomplished by the use of an Illinois chain grate stoker fed from a hopper, eliminating temperature fluctuations frequently caused where hand firing prevails.

In a control house located directly in the rear of the furnace, meters to each coil indicate the volume of distillate or petroleum passed, while indicating and recording gages give the amount of steam, oil and back pressure employed in the operation. This equipment affords visualization to the operator of the furnace and permits an adjustment of the important elements. In operation the oil is not all broken down into gasoline the first time it passes through the cracking coils, but after the gasoline is removed the residuum is rerun and this may be continued until the possibility of producing gasoline out of the particular material is exhausted. Usually it is found that this will occur with two reruns.

As a plant utility the Greenstreet process and apparatus can be, it is stated, of great service and value to the refiner. It is merely requisite to adjust the pressure, temperature and speed of the feeding of the steam and oil, to get a variety of results and enable the refiner to manufacture products for which at the time there is the greatest demand. If the demand for gasoline exceeds the demand for kerosene, the statement is made that it is only necessary for the refiner to put his kerosene distillates through these cracking coils and convert a large percentage thereof into gasoline. The process works with kerosene distillates as well as the heavier fractions of petroleum. On the other hand, if the refiner desires to make a lubricating stock he will extract only so much of the gasoline and lighter fractions as he desires and use a part of the residuum for making lubricating oil.

Attention is called to the statement that when the conditions of speed, pressure and sufficient steam are properly coordinated there is never any carbon formed in the Greenstreet cracking coils, and these correctly regulated conditions have resulted in commercializing the process.

The use of the " steam stilled synthetic crude gasoline " produced by this method and without refining or treating has in several instances been found, it is said, to be a most satisfactory and economical fuel for tractor motors.

The process also is claimed to be of value in that by its use some of the crude petroleum produced in the United States that now yields no gasoline, or such a small percentage by the usual methods as makes it unprofitable, can be made to produce a large percentage of gasoline. This was found to be the case, it is said, in treating what

is known as Caddo crude from the Red River district in Louisiana. This is a paraffin base crude out of which but little gasoline can be obtained by the usual methods, but which has a large kerosene content, and when treated by the Greenstreet process, is claimed to yield upwards of 60 per cent by volume of high grade, water-white gasoline.

The Gasoline Corporation [1] manufactures a product resembling crude petroleum and having cherry-red color and sweetish odor by cracking a hydrocarbon oil of a density of 32°–50° Bé. by heating it to 800° to 1500° F. (427°–816° C.) under a pressure of 80 125 pounds in the presence of steam. A colorless gasoline substitute distilling uniformly up to 410° F. (210° C.) and of a density of 50°–52° Bé. is said to be obtained from the "synthetic" product by distillation. The oil is pumped through pipes to preheating coils and cracking coils. Steam is admitted at the entrance to the preheating coils and the cracking coils, and is also mixed with the products issuing from the cracking coils. The products pass to expansion or gas chambers, whose purpose is to minimize fluctuations of pressure in the apparatus, and then through pressure-controlling valves to a condenser. The liquids from the condenser flow to a collector, and the gases are led to a scrubber through which flows a stream of naphtha, the products obtained by absorption being added to those obtained by condensation. It is preferred to operate on raw materials of narrow distillation ranges obtained by fractionating crude petroleum. Steam is used in the proportion of 1 to 6 or 8 of the distillate obtained. The product is fractionated in the usual manner up to 450° F. (232° C.) and the residue is subjected to a further cracking operation, alone or mixed with raw material. The distillate (benzine) is treated with sulphuric acid which is added in small portions at a time to prevent the temperature from rising above 60° to 70° F. (16°–21° C.) and is then washed with water, alkali, and water in succession, and distilled with steam in the usual manner. The cracking operation is regulated in accordance with the color of the drip and fume escaping from a valve at the end of the cracking coils. When the operation is satisfactory, the "drip," it is said, is cherry-red to light brown and the fume white; if the drip is black and the fume brownish, aromatic hydrocarbons accompanied by free carbon and gas are being formed. Deposits of carbon are removed from the interior of the coils by admitting air or other oxygen-containing gas through pipes, steam or similar diluting agent being simultaneously admitted to prevent overheating and destruction of the coils.

[1] Chem. Abs. 1918, 1833; British Patent, 115,014, Aug. 3, 1917.   (Greenstreet Process.)

Greenstreet [1] uses a steam pressure of about 100 pounds per square inch and an oil pressure (in the oil feed tanks) of 50 pounds. These pressures suffice to force the mixture of oil and steam through the cracking coil, which is one and one-half inches in diameter and one hundred feet in length (see Fig. 147) and is heated to a cherry red heat. A test burner situated at the end of the cracking coil is employed as a means of controlling the rate of feed of oil and of steam.

Operation is as follows: The furnace is first heated by means of crude oil supplied from the feed tank to a burner, where it is atomized by steam. Meanwhile, steam is being injected through the atomizer A and forced through the apparatus under pressure from the original source of steam. During this preliminary heating not only the temperature of the coil is raised, but the temperature of the condensing tanks is also raised. When the heating coil reaches a cherry red heat, one or both of the valves in the branch steam pipes B and C are opened to produce a pressure on the crude oil supply tanks, and either or both of the valves in the outlet pipes of these tanks are opened gradually to permit the oil to be forced into the atomizer. The oil thus atomized is forced under the pressure of the steam through a long cracking coil e where it is gradually transformed from heavier hydrocarbons into lighter hydrocarbons. This transformation is facilitated by the high temperature, the pressure inside the coil, the continuous smoothness of the interior of the heating coil and the uniformity of its cross sectional area.

The transformation of the heavy hydrocarbon compounds into lighter ones absorbs a considerable quantity of heat, and care must be taken to keep the temperature of the coil high enough to maintain the continuity of the process Although the whole coil may be a bright cherry red when the oil is first passed into it, the color of the inlet portion soon becomes dull on account of the rapid absorption of heat, even while the temperature of the furnace continues uniform Likewise, the transformation from a heavy hydrocarbon into lighter hydrocarbons causes an increase in the volume of vapor and, consequently, an increase in the pressure within the heating coil on account of the fact that the diameter of the heating coil is uniform. Considerable pressure is therefore required to force the material through the heating coil rapidly. This pressure will increase as the length of the coil increases and as its bore or internal diameter decreases.

Satisfactory results are obtained when the heating coil is a continuous pipe with an inside diameter of about an inch and one-half and of a length of one hundred feet, when the initial steam pressure is one hundred pounds per square inch, and the pressure on the oil in the feed tank is about fifty pounds per square inch, the temperature being cherry red.[2]

The temperature of the heating coil influences the products, but those which result from the treatment of given crude oil at a given temperature are of uniform quality. For instance, definite and uniform products can be obtained from

[1] U. S. Patent 1,110,924, Sept. 15, 1914; see also British Patent 16,452, July 13, 1912.

[2] See also U. S. Patents, 1,166,982, Jan. 4, 1916, and 1,110,923, Sept. 15, 1914.
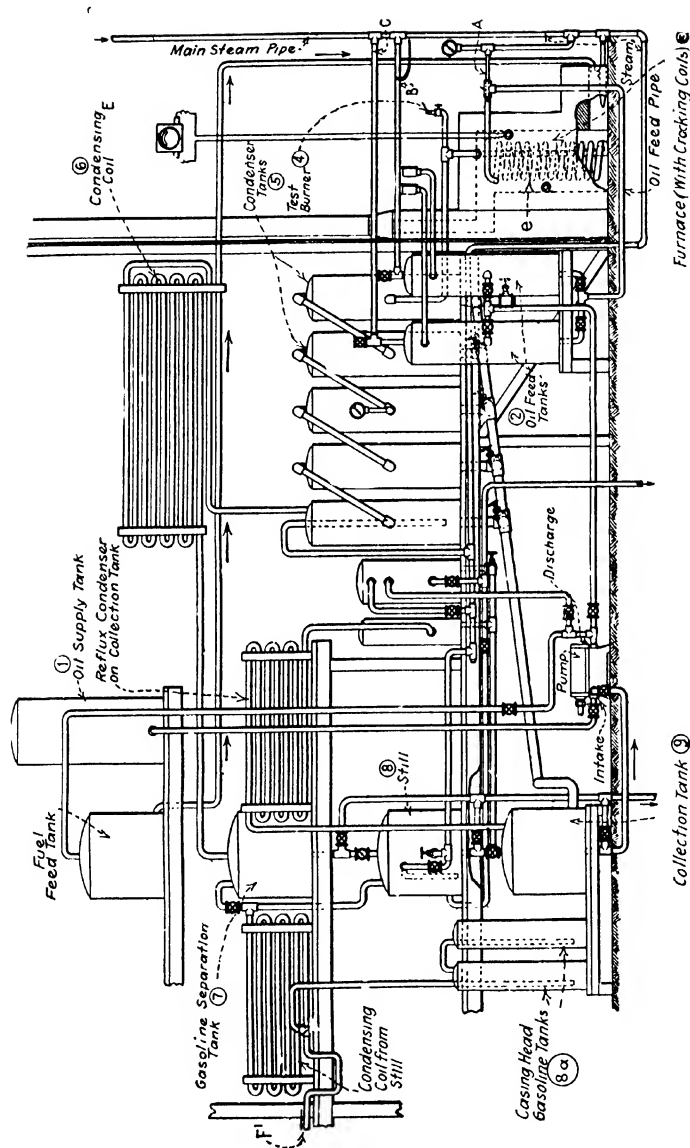
Fig. 147. — Diagram of Greenstreet process. (The numbers enclosed in circles indicate the course taken by the cracking stock and its products in passing through the apparatus.)

a given crude oil by treating at a red heat; whereas certain other products also of a definite and uniform quality will be obtained by treating another portion of the same crude oil at a bright cherry heat. The temperature may be varied, therefore, to suit the requirements of the desired product. The product resulting from the foregoing treatment is a mixture consisting principally of paraffins and olefins, the amount of the latter varying from a small percentage in the lighter gasolines and naphthas to as high as forty per cent or more in the heavier oils. The product is free from " grease " and is therefore regarded as suitable for cleansing purposes and for internal combustion motors. On account of its large content of olefins the gasoline produced is said to have a higher heating efficiency than gasoline produced by the processes commonly practiced.

As a matter of economy, it is desirable to limit the quantity of steam or water used in the process; and for determining the proper quantity of water and steam, a test burner is used. This test burner is connected to the delivery pipe of the heating coil. Initially steam alone issues from the test burner; but when the crude oil is admitted in gradually increasing quantity, the vapor resulting from it will issue along with the steam through the test burner. So long as the steam is largely in excess, the vapor issuing from the test burner will not burn with a steady flame; and consequently, the oil should be admitted in larger proportion to the atomizer until the vapor issuing from the test burner burns with a continuous flame. The test burner should be of the Bunsen type so as to insure a thorough commingling of air with the vapor before ignition. The proportion of oil can be increased until the test flame shows a tendency to a reddish or yellowish color, which color indicates a destruction of a portion of the oil. When this color indication appears, the proportion of oil should be slightly decreased until the test flame becomes bluish.

From the heating coil, the product passes into the first condensing tank, where the more easily condensable portion of the product is condensed. As the operation of the apparatus continues the condenser tanks gradually become hotter, so that a portion of the product which condenses in a given tank in the early period of the operation will distill over to the next tank at a later period of the operation. It is desirable to continue until the temperature of the last condensing tank is slightly in excess of the boiling point of water. From the last condensing tank, the product passes through the condensing coil E which is cooled by water; so that the resulting product which enters the gasoline separation tank is mostly gasoline and water. The water is drawn out from time to time from the bottom of the gasoline tank, and the gasoline is then passed into a still whereupon the connection between the gasoline tank and still is cut off. Live steam is then injected into the still with the result of vaporizing the lighter portions, which pass out into the condensing coil F. From the condensing coil F the gasoline passes to the delivery pipe F': but the lightest portion of the gasoline is trapped and escapes through a by-pass into the casing head gasoline tank where it is absorbed by heavy oil. After this distillation the operation is continued for some time, the water in the still tank is drawn off and the remaining contents are passed into the collection tank. From time to time the contents of one or more of the condenser tanks is drained into this collection tank. This tank is placed in communication with the supply pipe of the pump either alone or simultaneously with the main-supply tank, as desired; so that the contents of the collection tank are passed through the apparatus in the same way as the original supply of crude oil.

In operation, it is said that the inner surface of the heating coil soon becomes covered with an enamel or very smooth coating of magnetic iron oxide; and on account of the smoothness of this coating, it is believed to contribute to the value of the process in increasing the velocity of the vapors and by not affording any point where a deposit of carbon may be made. When the process is properly carried out, it is asserted that there is practically no formation of permanent gas and no deposit of free carbon, and as the condensable vapors liquefy in the condensing tanks, the last of which has a vent to permit the escape of the
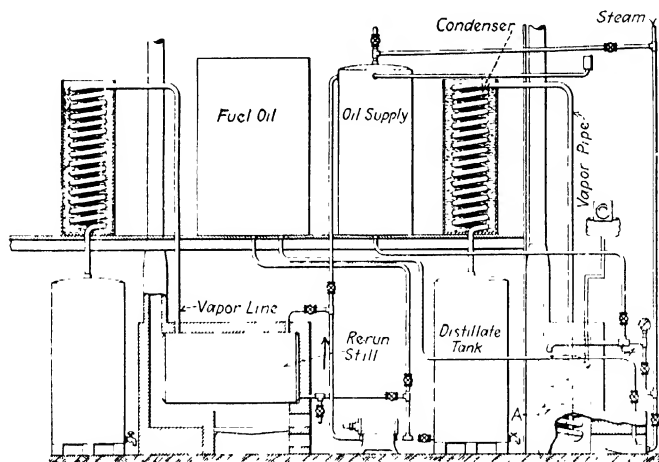
Fig. 148.

air initially contained, the pressure in the condensing tanks decreases from tank to tank until it is about the same as that of the surrounding atmosphere.

In one phase of his process,[1] Greenstreet re-runs the cracked product two or even several times at a "cherry red" temperature, in order to produce as large a proportion as possible of olefins. Steam is also used in this case, the steam being derived from a quantity of water about equal in volume to the volume of water used. Crude oil is stated to be the material used. The olefins obtained are alleged to be oxidized to manufacture alcohols.

The process consists in forcing the crude oil to and through an atomizer on the inlet side of a coil of pipe of uniform diameter kept at a cherry red temperature, the oil being thoroughly mixed at the atomizer with steam under a considerable pressure, about one hundred pounds per square inch. The quantity of steam is that of a column of water equal to or greater than the volume of the oil. In

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[1] U. S. Patent 1,110,925, Sept. 15, 1914.

order to increase the production of olefins, the product resulting from the treatment just described is itself submitted to the same treatment; that is, the condensate resulting from the passing of the crude oil through a long hot coil under the conditions above stated, is again passed through such a coil under the same conditions.

The mixture of paraffins and olefins is then treated with a sufficient quantity of sulphuric acid for the stated purpose of converting the olefins into the corresponding sulphonic compounds. Water is then added to convert these compounds, it is alleged, into the corresponding alcohols. In the meanwhile, the paraffins remain unchanged. For some purposes, it may be unnecessary to separate the paraffins from the alcohols. Usually, however, it will be desirable to separate the paraffins, and hence, Greenstreet subjects the mixture to fractional distillation. Distillation is claimed to be especially available for this separation on account of the fact that, whereas olefins and paraffins of substantially the same specific gravity distill at nearly the same temperatures, there is a wide difference in the distillation points of paraffins and the corresponding olefins on the one side compared with the alcohols derived therefrom. Thus, observes Greenstreet, the olefin C_8H_{16} distills at a temperature of one hundred and twenty-three degrees centigrade, while the corresponding alcohol $C_8H_{18}O$ distills at a temperature of from one hundred and eighty to one hundred and ninety degrees centigrade.

In another phase of the process, ordinary kerosene is run through at a rapid rate so as to convert it into an oil that does not leave a residue on evaporation,[1] without producing any material amount of naphtha. The lay-out of the apparatus is shown in Fig. 148. *A* is a coil of pipe in a furnace, heated with fuel oil. Steam pressure is maintained on the kerosene stock tank. The oil and steam mix in an injector and then pass rapidly through the coil. This is in the form of a helix, as shown. The temperature of the coil is maintained between 850° and 1150° F. (451° 621° C.). Under these conditions the following data are given, showing the desirable steam and oil pressures and the alternative lengths and sizes of pipe in the heating coil, corresponding.

Table 4. Showing Relation of Steam and Oil Pressures to Diameter, Length and Shape of Heating Coil, where the Temperature is about 1000° F. (538° C.).

	Size of Pipe	Length (Total)	Diam. of Helix	Oil Pressure	Steam Pressure
A.	1″	50′	15″	35–40 lbs.	45–50 lbs.
B.	$1\frac{1}{2}$″	100′	18″	50–60 lbs.	100 lbs.

The steam is claimed to be an essential factor in preventing cracking into naphtha. Under conditions as shown at *A*, Table 4, it is stated that the rate of flow of burning oil through the heating coil is 42 gallons (one barrel) every 6–9 minutes. The crude distillate is redistilled in the fire still up to 480° F. (249° C.) and any residue is added to the kerosene stock to be re-run. It is noted that starting with a burning oil of 45° Bé., the crude distillate should have a gravity of not over 46.5 Bé.[2]

[1] U. S. Patent 1,299,172, April 1, 1919.

[2] A furnace and special method for feeding it with powdered fuel is described in U. S. Patent 1,110,926, Sept. 15, 1914.

CHAPTER XVIII

CRACKING IN THE PRESENCE OF HYDROGEN, HYDROCARBON AND OTHER GASES [1]

Attempts to Hydrogenate Unsaturated Naphtha and Higher Boiling Oils, as well as Solid Substances, Coal, Asphalt, etc.

Since the day when Sabatier attracted the attention of chemists to the powerful hydrogen-carrying properties of catalytic nickel, there have been numerous suggestions directed to the hydrogenation of petroleum oils. Most of these have been offered without a full realization of the sensitiveness of catalytic nickel to various unfavorable conditions and particularly to the action of certain bodies which destroy catalytic activity. A considerable number of substances check catalysis of this kind, either wholly or in part. Arsenic, phosphorus and sulphur compounds often make their presence quickly evident. Such bodies, commonly termed catalyzer "poisons," have an important bearing on the hydrogenation of petroleum oils in which, for example, sulphur is a usual constituent.

There may be a future for the hydrogenation process in the treatment of cracked gasoline. In the refining of this product with sulphuric acid and alkali there is a shrinkage which although small in amount per barrel of gasoline so refined, yet constitutes a very substantial annual loss. In some investigations carried out by one of the authors a sample of cracked gasoline of a high degree of unsaturation, possessing a bad odor and brown color, was treated with hydrogen in the presence of a nickel catalyzer and afforded a well-saturated water-white product of sweet odor and stable for an indefinite period. No gummy deposit formed even on keeping for several years, while the unhydrogenated sample deposited a heavy layer of gum on standing only a fortnight.

The gases of a cracking plant contain large amounts of hydrogen and hence at a refinery cracking oil, the materials are available for hydrogenation.

There is, therefore, a possibility that hydrogenation may some day find a place in the oil refinery.

[1] Hydrogenation by means of steam has been repeatedly proposed. See Chapter XVI on processes using steam See also Lamplough, p. 269; Ellis, p. 279; Wells, p. 283; Nickel as a catalyzer, p. 318; McCarty, p. 419; Lidoff, p. 422; Maenichol, p. 424; Maxim, Standard Oil Co., p. 425; Day, p. 428; Danckwardt, p. 423 and Yunck, p. 470.

J. Winkler [1] reports negative results in attempting to hydrogenate
California oil distillates. Passing the vapors mixed with hydrogen
through hot tubes containing catalytic metals was attended with diffi-
culties, including the tendency of the oils to polymerize rapidly. This
difficulty was obviated by slow distillation, with excess of hydrogen.
The mixed vapors resulting from this distillation were passed through
a corona but, it is said, practically no chemical change was manifested
after this treatment.

A similar method was pursued, using the Birkeland-Eyde arc in-
stead of a corona. In this case the oils appeared to be decomposed
into non-condensable gases and a cloud of finely divided carbon. Di-
gesting with steam and aluminum dust under pressure is stated not to
be successful, also attempts to hydrogenate with reduced nickel. It
is suggested that hydrogenation could be accomplished catalytically
if the sulphur compounds could be suitably destroyed or their poison-
ing effect on catalyzers overcome.

Planes Limited and **W. P. Thompson** [2] distill petroleum oils under
pressure while agitating the liquid in the still with finely divided nickel.
Hydrogen is simultaneously supplied under pressure, which, in the
presence of the nickel, is said to combine with the unsaturated hydro-
carbons produced by the heat treatment. [3]

In Fig. 149 *A* is a high cracking still filled to the top of the direct fire-heated
portion with petroleum, the lower part *B* being made conical or tapering down to a
pipe *C*. *D* is a fire-grate, and *E* the chimney, *F* is the exit tube from the still,
having a valve *P*. This valve *P* is weighted to the required pressure required for
the best production of the particular hydrocarbon it is desired to produce. *K* is
the purifier. The shelves are charged with asbestos coated with finely divided
nickel *Q* is a two-way valve for temporarily passing the vapors at once to the
condenser when starting *J* is the exit for hot water from the condenser, and *I*
the entrance for cold water. *H* is the exit for the condensed products. *L* is a
separator in which the condensed liquid and the gases are finally separated. The
gases escape by the pipe *N*, and are injected into the fire, or if still very rich in
hydrogen are pumped back by the pipe *C* into the still. *M* is the exit for the
gasoline. *R* is a shot flask device for admitting the catalyst. *S* are accumulators
or sources of hydrogen, or purified water-gas under pressure, *T* is an accumulator or
other source of petroleum under pressure. *U* is a blow-off cock, *W*, non-return stop
valves, *X*, a stirrer driven by pulley *Z*, *Y*, a finely perforated rose in the still. It will
be noticed that the still *A* is naked for a large portion of its height. This is a
form of cracking still of a kind designed to enable the heavier hydrocarbons to
condense and descend and allow only the lighter ones to finally pass away.
Through flask device *R*, and the pipe *C*, the nickel catalyst (obtained by reduc-

[1] J. Frank. Inst. 1914 (178), 97–99.

[2] Chem. Abs. 1916, 273; U. S. Patent 1,160,670, Nov. 16, 1915; British Patent
5245, March 1, 1913; 21,273 (1913).

[3] See also J. Ind. Eng. Chem. 1913, 774.

tion of nickel oxide), is passed mixed with petroleum into the still, and from time to time the amount of oil in the still is kept up by fresh admission of petroleum through the pipe C, from the accumulator T. Through the pipe C also, hydrogen or water-gas is continuously passed from the accumulator S.

The petroleum is first purified from asphalt, sulphur, and other substances deleterious to the catalyst, which may be present before the material is introduced into the still. The hydrogen is also either pure hydrogen, or it has only such impurities as will not " poison " the catalyst. For instance, in place of hydrogen, purified water-gas may be used, but care must be taken that the water-gas is purified especially from tar and sulphur, and that it consists only or mainly of hydrogen, carbonic oxide and nitrogen.

The still is filled and kept filled up to the height of the heating chamber, with petroleum carrying 2 per cent of freshly made nickel catalyst, the hydrogen is admitted in a constant current, and the agitator put in motion. The pressure is kept at nearly atmospheric until the air is expelled through a cock W at the top. The cock is then closed and valve P is weighted to the usual cracking pressure, say 100 lbs. to the square inch. The higher the temperature up to 300° C. (572° F) and the higher the pressure up to that which the still will safely bear, and also the higher the index (n) of the carbon, the more rapid and complete is said to be the hydrogenation. Valve Q is turned to send the distillate through the purifier which
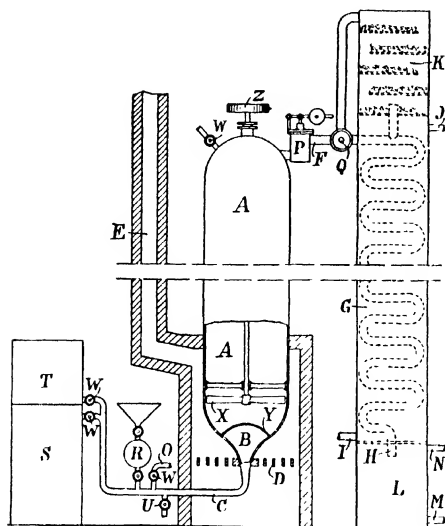
Fig. 149. — Apparatus for hydrogenating petroleum oils proposed by W. P. Thompson.

must be kept from the air, owing to the nickel being pyrophoric, and when gasoline begins to come over, purified water-gas (being much cheaper than hydrogen) can take the place of the latter. Saturated and unsaturated lighter hydrocarbons form and rise and they and the remaining petroleum are supposed to become more or less saturated with the hydrogen in presence of the catalyst. The heavier distilled vapors striking the cold upper portion of the still fall back to the lower part, while the lighter ones pass over to the condenser with the gases and are condensed, their place being taken in the still by additional petroleum. The petroleum during cracking is largely decomposed, and "is in a sort of nascent state," and therefore is asserted to be peculiarly sensitive to the action of the hydrogen, in the presence of the nickel. The unsaturated hydrocarbons formed while the lighter ones are cracked supposedly take up hydrogen, the pressure and vigorous agitation largely helping the action. In an ordinary cracking still where steam is used instead of hydrogen, the petroleum remaining in the still rapidly becomes heavier as lighter hydrocarbons are distilled off. In this case, however, the hydrogen is constantly combining with

the unsaturated hydrocarbons in presence of the catalyst and thus the remaining charge is claimed to be kept up nearly to saturation point, to be again cracked. After a time the petroleum gets too heavy to easily make gasoline. It is now run out from the still. The catalyst is separated by filtration and washing with a light hydrocarbon, and passed back into the still for further use. Eventually, however, the nickel begins to work very sluggishly. In such case, instead of being brought back into the still, it is washed with benzol as clear as possible from heavy hydrocarbons, calcined into oxide, or converted into nitrate or formate. It is then reduced by heating it in the presence of hydrogen to about 320° to 350° C. (608°–662° F.) for half an hour or more. The original catalyst is formed by reducing nitrate, acetate, or formate of nickel. It has been suggested to put formate of nickel direct into the still, and then precipitate it as an extremely fine powder in the mixed charge by means of heat.[1]

The **Badische Anilin und Soda Fabrik**[2] improves the quality of mineral oils by treatment in the liquid condition with hydrogen, at not above 200° C. (392° F.) under pressure, and in the presence of a catalyst, such as nickel, iron, cobalt, or copper, or mixtures of these.

L. Vignon[3] notes the formation of methane from water and carbon monoxide, by catalysis.

When carbon monoxide and water vapor are heated together to temperatures ranging from 500° to 1200° C. (932°–2192° F.) with various catalysts — iron, nickel, copper, silica, alumina, magnesia — there is always the formation of methane; sometimes in considerable quantity. In some cases there is an intermediate formation of carbides, which react with the steam; in others, hydrogen is produced, which in the presence of the catalyst reduces the carbon monoxide.

The **Badische Anilin and Soda Fabrik**[4] manufactures hydrocarbons, and oxygen derivatives of hydrocarbons by passing carbon monoxide and hydrogen, in the proportions of at least $\frac{2}{3}$ of a volume of the former to 1 volume of the latter, over a heated catalyst under a high pressure (exceeding 5 atmospheres). The preparation of hydrocarbons boiling from 20° to 250° C. (68°–482° F.), of olefins, paraffins, and benzene hydrocarbons, of alcohols, ketones (e.g., acetone), aldehydes (including acetaldehyde) and acids (e.g., acetic acid) is described.

N. Falk-Hultgren and **E. H. Vidstrand**[5] make a combustible liquid, similar to benzene, by heating a mixture of carbon monoxide or carbon dioxide and hydrogen to at least 2000° C. (3632° F.). In the reaction are formed, besides water, hydrocarbons, which condense

[1] See also **W. P. Thompson**, U. S. Patent 1,160,670, Nov. 16, 1915.

[2] J. S. C. I. 1915, 540; French Patent 472,776, May 28, 1914; Int. Conv. Sept. 1, 1913.

[3] J. S C. I. 1913, 817 and 742; Comptes rend. 1913, 157, 131–134.

[4] Chem. Abs. 1915, 2588; British Patent 20,188, Sept. 10, 1914.

[5] Chem. Abs. 1915, 2452 and 148; Danish Patent 18,827, July 11, 1913.

upon cooling to what is stated to be a readily volatile "benzene-like" liquid.

F. Sommer [1] states that aliphatic saturated hydrocarbons are obtained by subjecting polymethylenes or mixtures containing them, such as petroleum fractions and residues, to "cracking" and then converting the products into saturated hydrocarbons by reduction. The use of hydrogen and a catalyst, such as nickel, is mentioned as a suitable method of reduction. The low boiling point hydrocarbons obtained are reputed to be suitable for lighting and motor purposes.
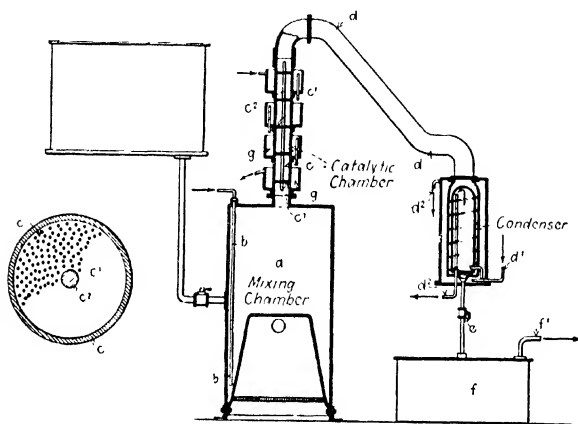
Fig. 150. — Method for subjecting oil vapor to the action of hydrogen, according to Brown.

M. A. H. de Dampierre [2] decomposes heavy oils such as crude petroleum, burning oil, naphtha and petroleum residues, into gasoline and other volatile oils by distilling in a still into which hydrogen is injected into the oil, and then passing the resulting mixture of oil vapor and hydrogen over nickel plates, the operation being effected under a pressure, e.g., 5–10 atmospheres. The products are led to a condenser. The nickel plates consist of perforated disks held in position in a vertical pipe by a central rod. The vertical pipe is also lined with nickel. A cooling system surrounding this pipe insures the return of heavy oils to the still.

E. Brown [3] vaporizes oil in a current of hydrogen and passes the mixture through a column containing transverse, circular perforated plates.

[1] Chem. Abs. 1915, 860; British Patent 19,772, Sept. 1, 1913.

[2] Chem. Abs. 1918, 222; British Patent 109,796, Aug. 15, 1917; French Patent 478,831, Feb. 22, 1915.

[3] U. S. Patent 1,225,569, May 8, 1917.

The apparatus used includes the still a (Fig. 150). A pipe b extends into the still and ends near the bottom for the introduction of a current of hydrogen. The vapor produced in the still escapes mixed with hydrogen at the top through a vertical conduit c in which are mounted nickel plates c^1 by means of a central rod c^2. The plates close entirely the conduit c, but they are provided with a great number of small holes allowing the vapor to pass. The vapor is thus obliged to come into direct contact with the surface of nickel and thus the catalytic action of the nickel is utilized. The wall of the conduit c is also internally covered with a layer of nickel. The upper end of the conduit c is connected through a pipe d to a condenser. At the lower part of the condenser, a cock e allows the volatile oil condensed to flow into a tank f, from the top of which the hydrogen which has been used for the treatment escapes through a pipe f^1 and is collected for use again. A water-cooling device g is mounted around the conduit c in order to maintain the temperature sufficiently low for insuring the total condensation of the vapors of heavy oil; consequently the heavy oil returns into the still a.

F. Bergius and J. Billwiller have found that at high temperatures and pressures, hydrogen causes a profound change in the properties of coal and bitumens, oil residues, heavy mineral oils and also carbonized substances in general. Coal, for example, in finely divided form is almost wholly converted into liquid products with only a small residue of the original substances. It is stated [1] that the coal is subjected to a hydrogen pressure of more than 40 atmospheres, and a temperature between 300° and 500° C. (572° 932° F.). Hydrocarbons are formed by chemical reaction between the hydrogen and the carbon compounds of the coal, which products are either liquid at ordinary temperature or have a low melting point. Only a very small portion of the carbon is volatilized in the form of methane at the working temperature which is below the coal distillation temperature proper so that practically no coal distillation products are formed. Notwithstanding this, the amount of liquid products formed is many times greater than that obtained by the usual coal distillation and reaches nearly 100 per cent of the carbonaceous substance of the coal, whereas the liquid products of usual coal distillation generally do not exceed about 3 per cent. The nitrogen contained in the coal is transformed during the hydrogenation process into ammonia and ammonium compounds and can be recovered in this form almost quantitatively.

Some of the organic compounds produced by the hydrogenation process contain oxygen and are of the phenolic type. The chief part is recovered as hydrocarbons of different boiling points, similar to

[1] J. S. C. I. 1915, 862; 1916, 167,732; British Patents 18,232 (1914); 5021, March 31, 1915; 4571, Feb. 21 (1914); U. S. Patent 1,251,954, Jan. 1, 1918; Swiss Patent 70,903, Nov. 16, 1915. See also Swiss Patent 71,808, Feb. 16, 1916, and Bergius, German Patent 290,563, Nov. 30, 1913; also Bergius, French Patent 470,551, April 6, 1914.

petroleum distillates. The unliquefied residue is a dark colored substance containing the ash of the original charge and a small proportion of carbonaceous material. The period of reaction can be shortened and the output increased if a hydrocarbon capable of dissolving or diluting the resulting products, for example a heavy commercial grade of benzol, is added to the dry material to be treated.
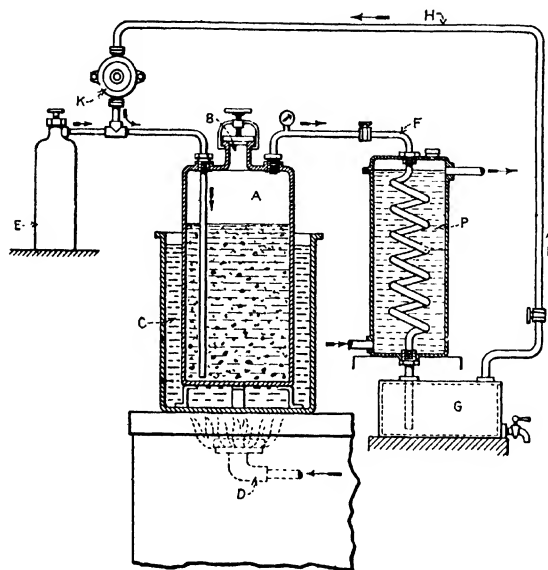
Fig. 151. — Method for hydrogenating coal at high pressures, according to Bergius and Billwiller.

The process is stated to be applicable not only to natural coal and other products of natural carbonization of wood and other vegetable material, but also to wood, peat and other vegetable material and to the products of coal distillation such as tar and pitch.

An apparatus is used which allows the treatment of coal under high pressure at an elevated temperature with hydrogen or hydrogen-containing gases or hydrogen-generating substances, that is to say, substances which are capable of liberating hydrogen under the operating conditions, like the hydrogen compound calcium hydride. In Fig. 151 A is a reaction vessel built to withstand high pressures. B is a charging orifice. C is a vessel surrounding the reaction vessel and filled with molten metal, the melting point of which is below the required reaction temperature. D is a furnace for heating the metal-bath vessel. E is a high pressure hydrogen container communicating with the interior of the reaction vessel by a conduit. F is an exit pipe leading to a coil which opens into a vessel G. H is a circulating pipe with a pump K. P is a cooler.

The operation is as follows:

The charging orifice of the reaction vessel is opened and the material to be treated placed in it. This material consists either of powdered coal, or of a suspension of coal in a diluent for the products of reaction. After filling the charge into the reaction vessel the orifice is closed pressure-tight. Hydrogen from receptacle E is introduced into the reaction vessel and the pressure brought to the desired degree. The furnace D is started and the metal bath C brought to the working temperature. The pump K is put in operation so that hydrogen is circulated through the reaction vessel and the material in it. The circulation of the hydrogen causes a stirring of the material under treatment. Under the effect of heat and pressure hydrocarbons are formed by reaction between the coal and hydrogen, and portions of these hydrocarbons are carried with the circulating stream through the coil P and are condensed. The condensed material accumulates within the vessel G. The uncondensed gas consisting nearly entirely of hydrogen is returned by the pump K to the reaction vessel. The consumed hydrogen is replaced by new gas taken from the receptacle E. Ammonia formed by reaction between nitrogenous bodies and hydrogen may be retained within the receptacle G by an absorbent.

Examples

1. Four hundred kilograms powdered coal are filled into a pressure vessel of about 400 liters capacity, which is connected to a tank in which hydrogen is held under 200 atmospheres pressure. After 15 hours the connection with the hydrogen tank is turned off and the vessel is emptied. About 10 to 15 kg. of hydrogen have been then consumed, according to the quality of coal used. From the contents of the vessel more than half of the coal can be separated from the solid residue as liquid. The remaining part of liquid products in the solid residue can be gained by extraction.

2. One hundred and fifty kilograms powdered coal are placed with an equal quantity of heavy benzol in a pressure vessel of about 400 liters capacity and this is connected to a hydrogen tank. For the purpose of better mixing, the vessel is either rotated, or the contents stirred and heated to 400° C. (752°F.). After 12 hours the vessel is opened and the liquid produced is separated from the solid residue. Only 15 per cent of the weight of coal employed is then left. The remaining 85 per cent is dissolved in the benzol. The consumption of hydrogen is about 5 kg.

3. Four hundred kilograms powdered coal are filled into a pressure resisting vessel of about 400 liters capacity and this is connected to a tank in which hydrogen is held under 200 atmospheres pressure and heated to about 400° C. (752° F.). After two hours the operation is interrupted and the material removed from the vessel. It contains only a small quantity of liquid substance, which is separated from the solid material. The solid material is extracted with an organic solvent such as benzene.

Heavy unsaturated oils, by treatment with hydrogen at high pressure and comparatively high temperatures [1] apparently become saturated, and at the same time a breaking down of the higher molecular weight bodies into those of lower complexity takes place. The process is an autoclave one and requires a range of hydrogen pressures from 20 to 100 atmospheres and temperatures between 200° and 500° C. (392–932° F.)

Day [2] describes a method of "saturating" an unsaturated crude petroleum or an unsaturated cracked distillate with hydrogen. This is said to be accomplished by first saturating a catalyzer (platinum or palladium) with hydrogen (or a hydrogen containing gas, such as ethylene) and then bringing the petroleum into contact with the catalytic substance in a special treating chamber under high pressure. The platinum or palladium becomes heated during its treatment with hydrogen or ethylene and this heat aids the subsequent hydrogenation or saturation of the petroleum oil.

Day states that he treats the oils with hydrogen gas or hydrocarbon gas or vapor, such as ethylene and its homologues, or gasoline vapors under conditions, such that the disagreeable odor is entirely or in a great part removed and the burning qualities of the oil in lamps is greatly improved. To effect this result, the oil, such as a distillate produced by high heat and the cracking operation or crude oil, is brought, together with hydrogen or an absorbable hydrocarbon gas or vapor, into the presence of a porous absorptive substance, such as palladium black or platinum sponge, porous zinc dust, fuller's earth, and other clays. By this means the desired purification and deodorization is said to be effected, probably by the direct addition to or combination of hydrogen or of hydrocarbon gas or vapor with the oil, wholly or sufficiently in part replacing the lacking hydrogen and converting the oil into a mixture of the marsh gas series of hydrocarbons.

The vessels are made of cast brass, tinned. The oil reservoir or tank A, Fig. 152 may be of any desired capacity and is provided with an oil inlet pipe a, having a valve a', and with an outlet-pipe a'', having a valve a''', and connecting with the treating or hydrogenating chamber B. This chamber is made strong and built to withstand a high internal pressure and is provided at one side or end with a filling opening f, into which is fitted a screw plug b. To another side or end is applied a gas cock b', having a screw threaded end for attaching a gas or vapor supply pipe. Another short pipe connection b'' is provided for attaching a pressure gage, and this pipe has a lateral cock b''' for connecting an air-pump or exhaust device. In the bottom of chamber B is a discharge-pipe c, having a valve c' and connecting with the oil receiving tank D. To the bottom of D is secured a discharge pipe d, having a valve e. The porous substance is saturated with hy-

[1] **Bergius**, J. S. C. I. 1915, 167; 1916, 528; J. Ind. Eng. Chem 1915, 1009, Chem. Abs. 1916, 2984, 1928; British Patent 4574, Feb 21, 1914; French Patent 470,551, April 6, 1914 (Int. Conv. May 5, 1913); German Patent 290,563, Nov. 30, 1913; Swiss Patent 71,808, Feb 16, 1916; Austrian Patent 71,208, June 26, 1916.

[2] U. S. Patent 826,089, July 17, 1906.

drogen or light hydrocarbon vapor or hydrocarbon gas under pressure, and the oil to be purified and deodorized introduced under similar pressure into the same flask or tank containing the porous substance. The improvement in the quality and odor of the oil is said to be quickly perceptible. The valve a''' being closed and valve a' open, the desired quantity of distillate oil to be deodorized and purified is supplied to tank A and then valve a' is closed. The screw plug b is removed and the desired quantity of catalytic substance, pref-erably palladium black or platinum sponge, is intro-duced through opening f into chamber B, the quantity being approximately in proportion to the quantity of oil to be purified. The porous substance is placed on a wire cloth screen or on layers of textile fabric. The palladium black or platinum sponge is used in the proportion of one-half ounce for each gallon of oil to be treated. The chamber B having been charged with porous material, the screw plug b is screwed into opening f, tightly closing it. The air in chamber B is now ex-hausted through cock b''' or it may be replaced by carbon dioxide or other noncombustible gas admitted through cock b' or b'''. Hydrogen gas or ethylene is now introduced under pressure through cock b' until the porous material is saturated, as shown by cessation of heat of absorption or by the greatly increased pressure indicated by a gage. The pressure of hydrogen may vary from normal to one hundred and fifty pounds per square inch or more. A practical pressure is fifty pounds to the square inch.

The porous substance having been saturated with hydrogen, the valve a''' is partly opened (valve a' being closed), permitting hydrogen to pass up into tank A till an equilibrium is established and then permitting oil to flow slowly from tank A into chamber B in contact with the hydrogen-saturated porous material. Valve c' is now opened, permitting the oil to filter through the porous substance, thereby becoming hydrogenated and deodorized. The purified oil is collected in tank D and may be drawn off as desired by opening valve c. Saturation or impregnation of the palladium black or

Fig. 152 — Device for subjecting oils to the ac-tion of hydrogen in the presence of catalyzers, proposed by D. T. Day.

platinum sponge with hydrogen is maintained by pumping in hydrogen-carrying gas or vapor through cock b' into chamber B. The gas may also be supplied under the pressure of generation or by pressure produced in any desired manner. The palladium black or platinum sponge is not consumed, and its use and action are continuous.

In case the porous absorptive substance becomes clogged with gummy or other residual matter this may be removed from the treating chamber or vessel and then subjected to a sufficient heat with excess of air to burn out the gum. When fuller's earth is used, it should be in much larger proportions than palladium black or platinum sponge, for example ten times the quantity of either of them. High pressure, and the temporary elevation of temperature due to pressure and rapid absorption of hydrogen (either alone or with absorbable hydrocarbons) facilitates the saturation.

The process is modified by placing the porous absorptive substance in a still and a crude oil or a distillate supplied to the still and subjected to distillation. During the distilling operation hydrogen gas or hydrocarbon vapors are passed through the body of oil and porous substance. An ordinary cylindrical still *H*, Fig. 153, is provided with a lid *g*, covering a hand-hole opening and the usual dome *g'*. At or near the bottom of the still is arranged a supply pipe *h*, having a perforated portion *h'* for introducing small streams of hydrogen carrying gas or vapor. Above this perforated pipe is supported a wire cloth or perforated plate partition *k*, upon which is placed a layer of porous absorptive material *m*. The porous material *m* having been placed upon the partition hydrogen carrying gas or vapor is admitted through the perforated pipe *h'* till the porous material takes up one thousand volumes or more of the gas or vapor. The charge of oil is now
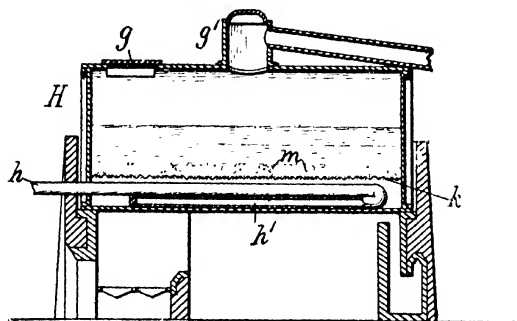
Fig. 153.

placed in the still and subjected to distillation, while at the same time streams of hydrogen-carrying gas or vapor are passed from the pipe *h'* through the body of oil and the porous absorptive material. The hydrogen carrying gas used may be a mixture of hydrogen and carbonic oxide. The best procedure is to let the palladium black take up the hydrogen (one thousand volumes or more at ordinary pressure and much more under greater pressures) and then filter the oil through the palladium black thus charged with hydrogen and subsequently pump in hydrogen to keep up the charge in the black.

An apparatus, said to represent an improvement over his earlier method, for attacking the problem of the "saturation" of unsaturated petroleum distillates is proposed by Day [1] and shown in Fig. 154.

An oil still *A* is set in a furnace and its opposite ends are provided with manholes and covers *a*, *a'* to give access for cleaning and repairing. Near the opposite ends of the still are secured transverse partition plates *B*, *B'*, forming vapor spaces *b* and *b'*, and a space between them for the oil to be distilled. The plate *B* does not extend to the top of the still. It is provided with a top opening *c* for the passage of oil vapor and hydrogen into the vapor space *b*; it is also provided near the bottom with a manhole and cover *b''*. The plates *B*, *B'* may be termed tube sheets and are connected by tubes *dd* for containing the porous catalytic material *e*.

[1] U. S. Patent 1,004,632, Oct. 3, 1911.

These tubes connecting with the plates B, B' constitute the " hydrogenator " D, the tubes being immersed in the body of oil which usually rises to the level indicated by dotted lines x. A perforated pipe F, having a valve f, extends longitudinally near the bottom of the still for admitting oil and hydrogen or either one alone, as required   With the outer end of pipe F connects an oil supply pipe F', having a valve f'; also a hydrogen supply pipe G having a valve g. A hydrogen generator H is constructed near the still, so as to supply hot hydrogen through pipes G and F. This generator may consist of retorts in which oil is decomposed for liberating hydrogen. The goose neck or vapor escape pipe J, having a controlling valve j, connects with the vapor chamber b' and with a condenser K. A pressure gage m is connected with chamber b' as a guide for properly adjusting
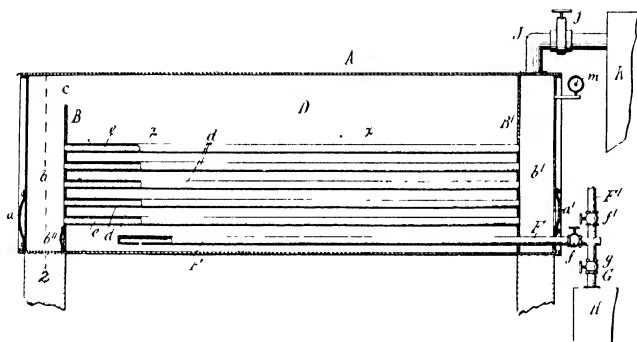
Fig. 154 — Method of treating oil vapors with hydrogen in the presence of catalyzers according to D. T. Day.

the valve j   The contact material, in the nature of a porous absorptive substance e, such as a finely divided metal or finely divided clay, is placed in the tubes d to nearly fill the same

The operation is conducted as follows: — Oil is supplied to the still, filling it to the dotted line x and when heated for the purpose of distillation, hydrogen or a hydrogen carrying gas is forced in through the perforated pipe F and passed up through the body of oil. The hydrogen and oil vapors, rising into the vapor space at the top of the still, pass through opening c into the chamber b and then through tubes d in contact with the porous absorptive material e, where the catalytic action takes place. The "hydrogenating" tubes being immersed in the body of oil which is being distilled are heated by the oil to a temperature as high as the distillation temperature of the oil, and for practical purposes they will be heated to a higher degree than the vapor, inasmuch as liquid from which oils are being distilled is always hotter than the distillate vapors passed off from it. By this means the hydrogen and oil vapor are superheated. The products now pass off into the outlet chamber b' through the goose neck J to the condenser K.

In order to regulate the temperature and maintain it at that degree most suitable to the contact process involved, the valve j is adjusted and set so as to increase the pressure, and, consequently, the temperature of the body of oil in the still. The temperature of distillation can thus be controlled. If the temperature of the body of oil is raised the hydrogen and oil vapors will be more highly superheated during passage through the tubes d. This is quite important

in order to control the operation of combining hydrogen with oil vapor. An attendant, by observing the pressure indicated in the gage *m* will understand how to adjust the valve *j* for producing the desired pressure and temperature in the still Hot hydrogen is passed from the generator *H* directly through the perforated pipe *F*, thereby aiding the heating of the oil. A stream of oil and heated hydrogen may be admitted simultaneously through pipes *F'* and *G* into pipe *F* and discharged into the still. If it is desired to increase the pressure and temperature of the hydrogen and oil vapor in contact with the process material *e* in the tubes *d* for increasing the "hydrogenating" operation, the valve *j* may be partially closed and adjusted so as to secure the desired effect.

Iron by hydrogen, zinc dust, reduced nickel or cobalt, dry porous clays, spongy platinum, or palladium, coating clays, or quartz, in fact any agent capable of bringing hydrogen into intimate contact with the petroleum compounds are mentioned as catalyzers. Whether the contact agent in some cases, as palladium, first forms a compound or alloy with the hydrogen, is immaterial to the final effect, which is that of yielding oil of better quality as the result of the contact action.

As an illustration of the practical operation of this process the tubes *d* of a still of 100 barrels capacity are first charged with briquets of copper or iron oxide mixed with metallic dust, the choice of the contact agent depending upon the market price of an available supply. The still is charged with Mexican crude oil of 16° Bé. gravity; the still is then heated until the first condensed vapor from the small amount of gasoline present in the crude oil, appears from the condenser, at the ordinary pressure of the atmosphere. Then hydrogen, as hot as possible, from the generator is passed in through pipe *F* at a rate that is averaged at 6 cubic feet per second. Inasmuch as this hydrogen is little purer than producer-gas and not of much value an excess is provided. The excess issuing with the vapors which at once begin to appear from the condenser, is usually fed to the fire under the still. In the case of oils of as high boiling points as that of 16° Bé gravity no extra pressure is used, unless the use of excessive hydrogen is undesirable. In that case the hydrogen will yield lighter products if the extra presssure goes to 50 pounds per square inch. In the case of lighter oils from California, Texas or other localities, extra pressure is employed to retard boiling of the oil until a suitable cracking temperature is reached, say 250° to 350° C (482°–662° F.) With the progress of the distillation crude oil is introduced in the manner described in order to maintain the level of the oil as nearly as may be until impurities collect and require interruption of the process for cleaning out the still.

W. Higgins and **C. H. Preston** [1] heat shale oil, crude naphtha, paraffin, or coal tar oil, or a mixture of two or more of these, in a converter under pressure, to such a temperature that the least volatile constituent is vaporized. The vapor is passed alone or together with hydrogen through a catalytic mass, such as a mixture of nickel oxide and pumice stone, and condensed in contact with the catalyst.

It is possible that heavy unsaturated oils nonvolatile at 150°–200° C. (302–392° F.) and free from catalyzer poisons may be treated with hydrogen in the presence of catalytic nickel to effect the saturation

[1] J. S. C. I. 1915, 1004; British Patent 23,876, Dec. 10, 1914.

of the oil.   An apparatus suitable for the purpose has been devised by
Ellis.[1]   See Fig. 155.

Oil is admitted to the tank A by pipe a to fill it one-half to two-thirds full,
for example to the dotted line.   Catalyzer is introduced, e g , by pipe a and hy-
drogen is entered by the pipe which is shown provided with the valve B to fill
one of the gas holders (e g., the holder C).   Hydrogen is forced from the gas-
ometer C into the gasometer D, by the way of the tank A, so that the gas bubbles
through the oil.   This operation is continued until all, or any desired proportion
of the hydrogen has been passed through the oil.   When the oil has been treated
to the desired extent, it is drawn off by valve E and the oil and catalyzer separated.
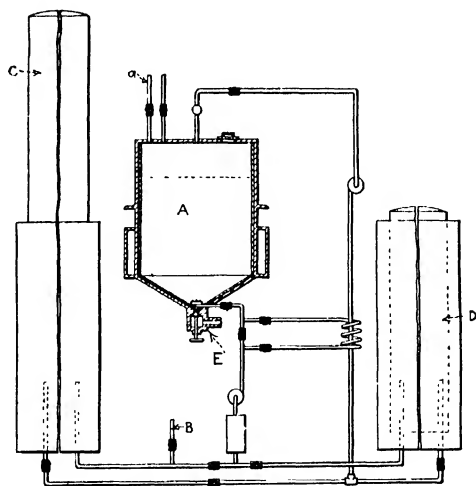
Fig. 155   - Ellis hydrogenating apparatus.

E. Jolicard[2] obtains liquid aromatic hydrocarbons from coal by
treating the latter in a furnace which is not externally heated, with
nascent hydrogen produced by introducing a mixture of superheated
steam and air at 500° C. (932° F.).   Carbon monoxide (in the form of
water gas or producer gas) at 600° C. (1112° F.) may be used in place
of all or a part of the air.

J. Holcgreber[3] mixes the vapors of petroleum or its distillates with
hydrogen and passes the mixture through metal tubes containing
metallic catalysts.   The tubes are heated to a temperature of 180°–
300° C. (356° 572° F.).   Benzene is said to be extracted from the
resulting vapors either by physical means or by combining it with alumi-
nium chloride.

[1] U. S. Patent 1,217,095, Nov. 20, 1917.
[2] French Patent 475,433, Feb. 17, 1914; J S C. I. 1916, 36.
[3] J. S. C. I. 1914, 17; French Patent 460,827, July 28, 1913.

Pirani (P. M. Justice) [1] mixes shale or coal in the form of coarse powder with a finely ground material, such as limestone, which under the action of heat will give off carbon dioxide, and with small iron scrap, and the mixture is slowly heated in a vertical retort to temperatures ranging from 175° to 800° C. (347° to 1472° F.) according to the oils required. The carbon dioxide given off during the distillation acts as a carrier for the hydrocarbon vapors evolved from the shale or coal, and is claimed to prevent them from becoming permanently fixed gases, while the action of the iron scrap increases the volume of hydrocarbon vapors given off in the retort. The proportions of the ingredients vary according to the amount of oxygen contained in the coal or shale. With an oxygen content of 6 to 13 per cent a suitable amount of limestone is 3 to 8 per cent and of iron scrap $1\frac{1}{2}$ to 4 per cent. When no more vapors are evolved the temperature is raised beyond 800° C. (1472° F.) and water in the form of a fine mist or jet is injected into the lower part of the retort. The vapors formed in the two operations are passed through a condenser, and any uncondensed vapors passed through an absorbing tower containing coke which has been saturated with a nonvolatile oil. The condensed oils are separated by fractional distillation. The residual oils from the various distillations may be mixed with fresh quantities of limestone and iron scrap and subjected again to distillation. The vapors formed in this operation are passed through a second retort exactly like the first, and at the same temperature, but charged to about half its capacity with manganese dioxide and iron scrap, in the proportion of 1 part of the former to 2 parts of the latter. The effect of these last-mentioned materials is to enhance the production of condensable vapors.

F. S. Low [2] sprays heavy residua characterized as fuel oil against a plate heated to a cracking temperature. This plate (Fig. 156) is heated independently of the other parts of the chamber which, as a whole, is kept below a cracking temperature by means of cooling coils. Fuel oil is charged into the lower part of the retort and is injected or forced through the nozzle A (Fig. 156). Steam or gas is used for this injecting process to start the apparatus working. Cracking takes place very quickly on the contact of the oil with the heated surface B, and since the rest of the apparatus is comparatively cool, vapors are removed from the heat zone before any secondary decomposition sets in. Unvaporized oil drops to the lower part of the retort and is again sucked up by the injecting nozzle and directed against the hot plate. A

[1] J. S. C. I. 1918, 363A; British Patent 115,573, Sept. 19, 1917. Appl. No. 13,485 (1917).

[2] J. S. C. I. 1916, 819; U. S. Patent 1,192,653, July 25, 1916.

sufficient pressure is built up in the apparatus and maintained in order to retard the formation of gas and unsaturated hydrocarbons. C is the relief valve for this purpose. Condensate collects in D and the gas formed is recirculated by a pump. It is said that the plate B is sometimes made of a catalytic metal, for example, nickel and in this case the apparatus is filled with hydrogen or " blau " gas for hydrogenating purposes.

Rough surfaces prolong the period of liquid contact somewhat. Where a catalytic effect is desired, the heated body is rough or porous to increase the surface. Terra cotta, pumice stone, iron, steel, nickel, copper, etc, may all be used and each exercises a specific effect. Iron and steel surfaces usually exercise a comparatively simple breaking down effect upon the oil molecules. Nickel, especially if freshly reduced, exercises for most purposes too much of a similar effect. Copper coated

Fig 156 -- Device for subjecting oils to the action of heated metals, and other bodies proposed by F. S. Low

with fine copper freshly reduced from the oxide is a catalyst intermediate between nickel and iron.

The Hydrogenation of Hydrocarbon Gases

C. Sprent [1] describes the production of ethylene from alcohol and the hydrogenation of the ethylene to produce ethane for refrigerating purposes, and points out the difficulties arising from the presence of contact poisons where hydrogenation with reduced nickel is involved. To make ethane **Sabatier** [2] passed a mixture of 2 volumes of ethylene and one volume of hydrogen through a tube one meter in length, containing freshly reduced and finely divided nickel; the gas on leaving the tube was passed through fuming sulphuric acid in order to absorb the excess ethylene. The resulting gas was then found to be pure ethane.

By means of the theorem of Nernst applied to the equilibrium, $C_2H_4 + H_2 = C_2H_6$, it may be shown that one volume of hydrogen can be added to an equal volume of ethylene in such a way as to leave practically no remainder of either of the gases of the left side of the

[1] J. S. C. I. 1913, 171.   [2] Chem. Zeit. 1907, 1096.

equation. It is merely necessary to find the right catalyst and conditions for the desired result. Simple though this reaction appears, the production of ethane in quantity was found to be a difficult matter, requiring for its completion as a rational process a thorough investigation and the application of very different methods than would have been supposed necessary.

The chief difficulties encountered can be placed under two heads, first the production of pure ethylene, and secondly the quantitative saturation of one volume of ethylene by one volume of hydrogen.

As regards the former of these, the method used was fundamentally that of **Maihle** (passing the vapor of alcohol over aluminium oxide according to the reaction $C_2H_5.OH = C_2H_4 + H_2O$). **Maihle** [1] showed that the catalytic action of the aluminium oxide was not only dependent on the temperature but also on the physical structure of the catalyst, an amorphous oxide giving a good yield of ethylene, and the crystalline oxide a poorer one. In these experiments the same phenomena were very often observed; many samples of alumina gave no ethylene whatever, but converted the alcohol into an oily substance. The catalytic value of any sample of alumina can be tested to some extent by shaking the oxide with distilled water. The active samples treated thus are converted partially into a colloid, the particles of which move towards the cathode when subjected to an electric current. The particles of inactive samples immediately fall to the bottom of the vessel.

Great care must be taken to keep the reaction at the temperature at which the yield of ethylene is at a maximum, namely, 360° C. (680° F.). If the temperature be raised the ethylene commences to decompose, forming hydrogen, methane and carbon, and, moreover, the yield of gas decreases, on account of the amorphous oxide being slowly converted into the crystalline state. The high temperature also affects the catalyst in such a way as to alter the nature of its reaction with the alcohol. Thus, aldehyde and hydrogen can be evolved by the decomposition of the alcohol.

On the other hand, the temperature should not be allowed to fall below 360° C. (680° F.); because not only does the amount of ethylene then decrease, but a considerable amount of ether may in this way pass into the ethylene. The ether is formed by a primary decomposition of the alcohol, which takes place at a temperature of about 230° C. (446° F.) The ether itself, however, is also decomposed, forming ethylene and water at a temperature of 300° C. (572° F.). Unless the temperature of the whole apparatus where the gas is generated is kept at 360° C. (680° F.), a portion of ether may pass through with the ethylene without forming ethylene. The reaction takes place, it is said, in two phases,

$$2C_2H_5OH = (C_2H_5)_2O + H_2O$$
$$(C_2H_5)_2O = 2C_2H_4 + H_2O.$$
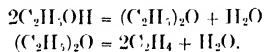
It was found especially in an apparatus on a large scale that the ethylene always contained some ether, sometimes as much as 10 per cent This fact is lost sight of in the laboratory if the gas is collected over water, or the usual solutions used for the determinations of the gases by absorption. The formation of the ether can be reduced to a small percentage, if the oven in which the reaction takes place be

[1] Chem. Zeit. 1909, pp. 18, 29, 242, 253.

placed in a lead bath and the alcohol vapor heated to a temperature of 360° C. (680° F.) before being passed through.

For the production of ethylene in quantity, iron tubes 3 inches in diameter and 1½ meters in length were employed; these were fitted inside with suitable contrivances to hold the catalyst. The tubes were connected with the vessel in which the methylated spirit was evaporated.

Ethylene produced in this way is not, however, suitable for the synthesis with hydrogen to form ethane, as it contains impurities which on coming in contact with the finely divided nickel bring about a decrease of the catalytic activity of the nickel, and if the process is continued, eventually cause it to become entirely inactive. The elimination of these disturbing impurities formed the chief difficulty in the beginning of the experiments described. First it was found necessary to eliminate the ether and traces of other impurities such as aldehyde, isoprene, etc., by compressing the ethylene up to about 50 atmospheres. In this way the impurities were condensed and could be removed by a suitable arrangement of the apparatus. If these impurities were allowed to pass into the nickel oven not only was the catalytic action impaired, but the gas was made impure by the products of decomposition of these substances. The ethylene thus treated was also found to contain traces of sulphureted hydrogen, arising from the presence of sulphates in the alumina. This impurity was removed by passing the gas through a solution of lead acetate. A further washing of the gas with concentrated sulphuric acid was found essential; Certain impurities, the nature of which was not determined, and which acted as poisons to the contact substance, were eliminated by this treatment.

The ethylene purified in this way was entirely free from any impurity having a weakening effect on the catalyst. The hydrogen used was a product of the alkali works of " Griesheim-Elektron " in Bitterfeld and was so pure as to require no further treatment. The two gases, ethylene and hydrogen, were mixed in equal volumes, the adjustment being made with the aid of the gas-mixing and measuring apparatus known as the " Rotamesser," and then allowed to pass into the tube containing finely divided and freshly reduced nickel. This tube was constructed similarly to the one used for ethylene, only here the tubes were only one meter in length and four in number. The first two were coupled parallel with one another, the gas leaving each of these combining and passing into two or more similar tubes coupled one behind the other. The dimensions of the tubes were determined by experiment, so that with the gas-velocity used (2 cu. m. per hour), the temperature arising from the formation of the ethane (the reaction is exothermic), was unable to reach the point at which ethane decomposes, on

account of the radiation of the heat. Working with the same gas
velocity and a greater diameter of the tube, it was necessary to cool
the interior by means of water pipes.

The necessary temperature of 200° C. (392° F.) can be kept up with very little
external heating. The difficulty, however, was that under no conditions of tem-
perature, or by means of any arrangement of the contact substance in the oven,
could the reacting gases be made to unite quantitatively, the best result obtained
being a percentage of 10 per cent ethane in the gas formed. This became a very
acute difficulty, as chemical methods of removing the hydrogen and ethylene
proved impracticable.

The next step was to employ an air-condensing apparatus (Linde's system),
used for the production of oxygen, and attempt to separate the ethylene and hy-
drogen from the ethane by means of rectification. This proved only a partial
success, as only hydrogen could be eliminated, the ethylene remaining with the
ethane. The rectifying column of the machine worked under pressure from 3–5
atmospheres, and it would have been possible, it is said, to get a better result had
there been another column where the liquid gases had been under a pressure of
only a little more than that of the atmosphere. In fact it was shown that the
liquid gas mixture, after standing some time in a Dewar flask, contained only one
per cent of ethylene.

The solution of the problem was only arrived at when it was decided to effect
the combination of the two gases under pressure. According to the law of Le
Chatelier, it was clear that pressure must have a beneficial effect, but in considera-
tion of the sudden rise of temperature occasioned by the combination of so much
gas in the small oven, it seemed unavoidable that the temperature should rise
above the temperature of decomposition of ethane. Moreover, a polymerization
of the ethylene seemed possible.

Experiments showed that the combination of equal volumes of
ethylene and hydrogen under pressure in this way was impracticable,
owing to the sudden rise of temperature, making a proper control of the
apparatus uncertain and precarious. However, by passing the gas
mixture containing 80 per cent ethane, 10 per cent ethylene and 10 per
cent hydrogen at a pressure from 30–40 atmospheres through an iron
autoclave filled with nickel pumice stone, a complete success was at-
tained, the resulting gas being pure ethane.

The 80 per cent ethane gas mixture, produced in the way men-
tioned above, was collected in a gasometer, and needed only to be
drawn off by means of a gas compressor, that forced the gas through
a second tube which, as already stated, was held under a pressure of
from 30 to 40 atm. From there the gas passed through the condenser
into the steel cylinder, where the ethane was liquefied and weighed off.

A careful adjustment of the " Rotamesser " measuring the volume of the two
gases at the commencement of the process is necessary as an excess of one or the
other of these gases naturally detracts from the purity of the ethane. The error
in this case must be corrected by an addition of the required amount of one of the

gases to the gasometer containing the ethane gas mixture. It is advisable to work with a slight excess of hydrogen in order to avoid disturbances of this kind, as the hydrogen can always be " blown off " by opening the valve of the cylinder containing the liquid ethane. In the case of ethylene this is not possible. The process here described runs continuously, and with the trial plant set up in Bitterfeld, 25 kilos of liquid ethane were made daily.

Eldred and **Mersereau** [1] control the catalytic reduction of acetylene to ethylene by the use of an inert diluent gas, particularly carbon dioxide. Nickel and palladium on petroleum coke is given as one of the catalysts used.[2]

The reaction between carbon monoxide and steam to produce hydrogen is said to be facilitated by the use of lime.[3] Water gas or other gas rich in carbon monoxide is mixed with steam and the mixture is passed over lumps of calcium oxide, arranged in superposed layers in a vertical tower and maintained at a temperature of 400°- 750° C. (752°-1382° F.) by heat initially supplied by the gas and by the heat of the reaction. This would have a bearing on those cracking methods wherein carbon monoxide is produced in the presence of steam and lime.

Oil gas is manufactured by the **Hollandsche Residugas Maats-chappij** [4] by cracking liquid hydrocarbons in generators and treating the residual hydrocarbons directly without previous heating, with hydrogen or gases containing hydrogen to form new paraffins.

R. C. Downing and **E. F. Pohlman** [5] have studied cracking of gas oils in various atmospheres. The atmospheres used were nitrogen, carbon dioxide, carbon monoxide, hydrogen, methane, blue gas, and a mixture of blue gas with 10 and 20 per cent of steam respectively. The effect of each diluent on candle-power of the gas, candles per gallon, B.T.U. per gallon, and the production of gas, tar, and carbon was studied. With nitrogen the calorific power of the gas per gallon of oil was 97,000 B.T.U. at 1350° F. (about 730° C.). This is slightly better than is obtained in atmospheres of carbon monoxide, carbon dioxide, and methane, and lower than in hydrogen or blue gas. The amount of tar and carbon produced was considerable, as is more usually the case in inert atmospheres. The yield of oil gas by weight was rather low. In an atmosphere of carbon dioxide the volume of the gas made

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[1] U. S. Patent 1,308,777, July 8, 1919.

[2] See also Chem. Abs. 1919, 2218.

[3] **P. Siedler** and **K. Henke,** Chem. Abs. 1916, 1708; U. S. Patent 1,181,264, May 2, 1916.

[4] Chem Abs. 1917, 2729; Norwegian Patent 27,930, May 21, 1917.

[5] J. S. C. I. 1917, 125; 1916, 917; Amer. Gas Institute, Gas J. 1917 (137), 24–26.

was over 60 cubic feet per gallon of oil, and it contained much hydrogen and méthane. The production of carbon was much increased. The reaction $2CO_2 + C_2H_4 = 4CO + 2H_2$ probably occurs, it is said, to a slight extent. With hydrogen, gas of high calorific power tends to be produced, owing to the production of saturated compounds. There is a decrease in the formation of tar and carbon. The production of illuminants is low; apparently some of the unsaturated compounds are hydrogenated. Methane acts very much like an inert atmosphere; much less methane is actually produced from the oil, but the production of hydrogen is larger, due probably to the decomposition of the methane. The effect of blue gas was studied in some detail. The conclusion is reached that no advantage is to be gained over blue gas by the use of any of the above-mentioned atmospheres alone. Blue gas gives much better candle-power results than either hydrogen or carbon monoxide. Tar formation is lowered and the deposition of carbon is about the average. Steam lowers the candle-power and candles per gallon, but raises the B.T.U. per gallon of oil, possibly due to formation of hydrogen by partial decomposition of the steam. With carbon monoxide great loss of candle-power was noticed, due to the large proportion of carbon monoxide in the finished gas. The B.T.U. results were the lowest obtained with any atmosphere except from oil used alone with a much longer time of contact. More tar was produced with carbon monoxide than in any other atmosphere. Carbon monoxide moreover seems to prevent the decomposition of the " illuminants."

Whitaker and **Leslie** [1] have studied the decomposition of a vaporized paraffin hydrocarbon oil (specific gravity 0.8, boiling point 150° 265° C. (302°-509° F.) at atmospheric pressure and at temperatures of 621°, 725°, and 825° C. (1150°, 1337°, and 1517° F.) respectively, using the electrically-heated furnace described by **Whitaker** and **Alexander,** [2] and the effect of varying the oil feed and of adding hydrogen at different concentrations (approximately $1H_2 : 2$ oil gas and $2H_2 : 1$ oil gas respectively) was investigated. When oil is cracked in an atmosphere of hydrogen, the absorption of hydrogen is greater the higher the concentration of the latter, the higher the temperature and the lower the rate of oil feed. There is no marked difference in the amount of tar formed in the presence or in absence of added hydrogen below 723° C. (1333° F.). At 825° C. (1517° F.) less tar is formed when hydrogen is added. The proportion of tar increases with decrease of temperature, and with increasing rate of oil feed, particularly at the lower temperatures. Below 723° C. (1333° F.) the tar formed consists largely of

[1] J. S. C. I. 1916, 955; J. Ind. Eng. Chem. 1916 (8), 593–601, 684–695.

[2] J. S. C. I. 1915, 705.

unchanged or partially changed oil. The proportion of the carbon of the oil which appears as hydrocarbons in the gas is largely increased by addition of hydrogen. The volume of illuminants produced per unit volume of oil increases, in general, it is said, with the temperature. About one-third by volume of the illuminants in the gas is stated to consist of propylene and higher olefins. The formation of ethane is not large at any temperature, but the formation of methane is greater the higher the temperature. A decomposition temperature of about 825° C. (1517° F.) appears most desirable provided too great opportunity for extensive secondary and tertiary changes is not given.

Rather and **Reid** [1] have hydrogenated ethylene and observed the rate of the reaction. The mixture of the volatile substance (vapor or gas) and hydrogen is passed through a nonvolatile, inert liquid containing the catalyst. The rate of hydrogenation of ethylene at 180° C. (356° F.), using a nickel catalyst in melted paraffin medium, was found to be regular for a gas mixture containing 10 per cent ethylene, but irregular for richer mixtures; the determining factor is considered to be the solubility of the ethylene and hydrogen in the paraffin.

Lane, Ryberg and **Kinberg** [2] note that the addition of hydrogen to acetylene and ethylene through the catalytic action of nickel, copper, etc., is best carried out by adding hydrogen gradually to the unsaturated hydrocarbon in order to prevent so great a rise in temperature as to bring about injurious side reactions.

C. Paal and **A. Schwarz** [3] have found that ethylene when mixed with an equal volume of hydrogen is slowly reduced quantitatively to ethane at the ordinary temperature on the addition of a solution of colloidal platinum. The velocity of the reaction within certain limits is only slightly dependent on the concentration and amount of colloidal platinum present. A colloidal solution of platinum requires about twice as long to bring about complete hydrogenation as a colloidal solution of palladium of equal strength, while, with colloidal solutions containing atomic proportions of palladium and platinum, the former is slightly more active.

Paal and **Hohenegger** [4] have made numerous experiments on the reduction of acetylene by hydrogen in presence of colloidal palladium, partly in a gas burette, partly in a vessel which could be shaken, and partly in an apparatus in which the gases could be circulated. The

[1] J. S. C. I. 1915, 1072; J. Am. Chem. Soc. 1915 (37), 2115–2118.

[2] Seifen. Ztg 1913, 1035; German Patent 262,541, 1910.

[3] J. S. C. I. 1915, 851; Ber. 1915, 48, 994–1001.

[4] J. S. C. I. 1915, 574; 1913, 186; Ber. 1915, 48, 275–287; J. Chem. Soc. 1915, 108, i, 113–114.

chief result was the demonstration of the influence of the adsorption of acetylene by palladium on the course of the reaction. Starting with equal volumes of acetylene and hydrogen, and with a fresh palladium solution, so much of the former gas was adsorbed by the colloid and chemically changed, in all probability polymerized,[1] that the hydrogen was really present in excess, with the result that varying volumes of ethane were formed and some acetylene remained unchanged. This is probably the reason why in previous investigations on the catalytic reduction of acetylene the chief product was always ethane, even when insufficient hydrogen to complete the first stage reduction to ethylene was employed. When the colloid has been in contact with acetylene, it loses the power of adsorbing the gas and the yield of ethylene increases. Indeed, with a slight excess of acetylene, all the hydrogen may be used in the formation of ethylene.

The mixtures of gases were analyzed as follows:

The two unsaturated hydrocarbons were absorbed by bromine water and the acetylene estimated separately by an approximate method [2] in which an ammoniacal silver solution was used as the absorbent. Hydrogen was estimated in the residue by absorption with palladium hydrosol and sodium picrate [3] and the ethane (and impurities) measured by difference.[4]

Thermolyzation and Distillation of Oils and Gases in the Presence of Natural Gas, Hydrogen, Ethylene, etc.

Kidd [5] found that in attempting to make illuminating gas from tarry materials, e.g., coal tar, by passing through heated retorts, that a great deal of carbon was produced. To decrease the carbon deposit and increase the yield of gas he carried out the process in the presence of petroleum naphtha vapor, and superheated steam.

E. W. Tait [6] mixes kerosene or higher petroleum fraction with natural gas, thermolyzes the resulting mixture, and cools the products. Thermolyzation and condensation take place under pressure.[7]

Naphtha, kerosene, or other of the higher paraffins, is mixed with natural gas. The natural gas may be introduced into a tank, still, worm, or coil of pipe, either at the natural rock pressure from the well, or it may be forced into the reaction vessel by means of a pump or

[1] J. S. C. I. 1913, 186.

[2] Hohenegger, Diss. Erlangen, 1912.

[3] J. S. C. I. 1910, 236.

[4] See also Karo, Ger. Pat. 253,160; J. S. C. I. 1913, 109.

[5] U. S. Patent 124,441, March 12, 1872.

[6] U. S. Patent 1,069,908, Aug. 12, 1913.

[7] This process suggests partial similarity in some respects with Hall's compression method.

compressor. The heat applied varies from about 200° F. upward, depending on the quality of the natural gas used, the specific gravity of the higher paraffin used, and on the desired specific gravity of the product. The relative amount of the higher paraffins to the volume of natural gas used depends on the desired specific gravity of the product (for instance, if the quantity of the naphtha kerosene, or other higher paraffins in proportion to the quantity of the natural gas used is diminished, the product becomes of lower specific gravity). The mixed vaporized hydrocarbons are then condensed.

In Fig. 157, A represents the gas inlet from the well, and if the natural pressure is not sufficient to give a free circulation through the system, a compressor B operated by an engine C is used, which also actuates a pump D in connection
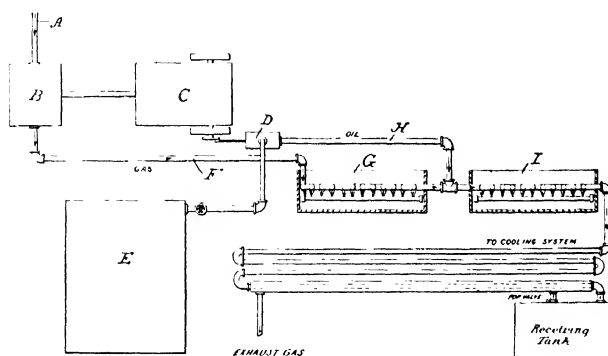
Fig. 157. — Apparatus for heating oils with natural gas, according to E. W. Tait.

with an oil tank E. The gas flows or is forced through a pipe F, and in its passage is subjected to the heat of a burner G, and is mixed with oil passing through the pipe H. From this point the mixed hydrocarbons pass through a pipe which is heated by a second burner I, and then through the condenser. The condensed hydrocarbon liquid passes into the receiving tank.

If there is not sufficient natural pressure from the gas well, compressor B should compress the natural gas taken into the system to a pressure of about 50 pounds per square inch, sufficient to cause a free circulation through the system. The natural gas travels through the coil G at the rate of 5000 cubic feet per hour. The coil or worm G is composed of a pipe two inches in diameter and about 200 feet in length. In the coil or worm G the natural gas is heated to about 500° F. (260° C.). The oil or higher paraffin is pumped into the natural gas at the rate of about 60 gallons per hour. The coil or worm I is composed of pipe two inches in diameter and about 300 feet in length. The temperature of the material in the coil I is maintained by means of the burner at about 300° F. (149° C.). The cooling system is composed of pipe two inches in diameter and about 1000 feet in length, of which the last two hundred feet are incased or jacketed. The pop valve on the receiving tank releases the unconsumed gas when the pressure in the receiving tank reaches 50 pounds per square inch.

Leffer [1] uses an inert gas under pressure to carry the vapors from a still to the condenser, so as to prevent further decomposition of the light oils produced. The pressure of the inert gas also raises the boiling point of the oils in the still.

The operation is effected under three combined conditions, viz., the accurate regulation of the pressure of the pressure medium, the constant circulation of the pressure medium and a working temperature not exceeding a maximum of 410° C. (770° F.). When the process is carried into effect under all these conditions, it is stated that the quantity of distillate obtained will be large. The substance being distilled is subjected to agitation either by means of stirring vanes or by blowing the pressure medium through the substance (See Fig. 158.)

a is the distilling vessel, h the vapor line, b the condenser, c the collecting vessel for the distillate, i a tube which is connected to a suction or force pump d from which it continues to conduct the pressure medium to the retort, s the stirring vanes rotated by means of the pulley r for

Fig. 158. — Pressure still with means for circulating a permanent gas, proposed by Leffer.

agitating the substance to be distilled. z is an inlet pipe provided with a cock for the pressure medium.

The distillation proceeds in the following manner:

The hydrocarbon in the retort a is evaporated and decomposed by heat, condenses in b and is collected in c, while the pressure medium under the action of the pump d is again forced into the retort a from which it carries away the lighter products which are formed. Hydrogen, nitrogen, carbonic acid gas, methane or gases obtained from the distillation itself are used to create pressure. Suppose that the initial material is gas oil, a petroleum distillate of specific gravity 0.871, and that from it is obtained the following results on fractionating: up to 265° C. 1 5 per cent, up to 300° C 14 per cent, and the remainder only after exceeding 300° C. 6000 grams of initial material were treated and a pressure of between 11 and 12 atmospheres developed in the apparatus by means of nitrogen; the temperature rose after the heating to about 408° C. and dropped slowly to 375° C. The distillate amounted to 4007 grams or 67 per cent; the residue to 1380 grams or 23 per cent, and the gas about 10 per cent. The fractionating of this distillate yielded 14 per cent passing over between 46° and 90° C., 16.5 per cent up to 125° C., 12.5 per cent up to 150° C. and the remainder up to

[1] British Patent 2328, Jan. 29, 1912. See also French Patent 439,476 (1912); British Patent 4140 (1913); French Patent 454,580, Feb. 19 (1913)

250° C.   Care should be taken that the supply of the pressure medium is stopped as soon as the pressure of the gases developed within the apparatus reaches the necessary amount, the pressure being then cut off and the gases generated caused to circulate by means of the pump.

An independently heated cracking chamber [1] and reflux condenser, interposed between the still a and condenser f, is said to provide a more complete control of the cracking conditions.

Heinemann [2] reports success in causing the union of acetylene with methane, producing in this way good yields of propylene.   He uses a catalyzer which is a combination of a base metal (copper, aluminium, magnesium) with a rare metal (platinum or palladium).

The contact bodies may be prepared in the following manner: One of the common contact metals, for example copper, is deposited in a porous body, for example pumice stone, either electrolytically or by the reduction of a copper salt. The pumice stone provided with a coating of copper or having its pores partly filled with copper is dipped in a solution of a salt of a rare contact metal, for instance chloride of platinum, and is dried.   The salt is then, if necessary, reduced. In this way there is obtained a contact body consisting of two metals which exert a mutual balancing effect on one another, the more active property of a rare metal being mitigated by the less active property of the common metal.   The common contact metals can also be used in a finely divided state or in strip form, for example copper gauze, copper wool, aluminum turnings or magnesium strip. These metals are then prepared by dipping in a solution of a salt of a rare contact metal, such for example as a chloride of platinum or palladium.   The rare contact metal is then deposited by electrolysis   Care must however be taken to immediately wash and dry the contact bodies so prepared in order to avoid destruction of the common metals.

The process is carried out in the following manner. Equal quantities of acetylene and methane are mixed together and passed through heated tubes or vessels containing one of the above described composite catalysts.   The temperature employed varies from 100° 200° C. (212°–392° F), according to the contact metals employed.   The heating of the spaces in which the reaction takes place can either be effected by the application of heat to the exteriors of the tubes or vessels containing the contact bodies or by passing a current of electricity through coils placed in the tubes or vessels   The use of inert gases, as carbonic acid gas or nitrogen, is recommended, in order to remove the oxygen present at the commencement of the process in the reaction tubes or vessels.   The two gases unite to form propylene with a yield said to be approximately 70 per cent.

R. B. Day and **D. T. Day** [3] bring hot gases of combustion, practically free from oxygen, directly into contact with oil in a pressure chamber lined with fire brick.   As shown in Fig. 159, oil and water are sprayed into the cracking chamber A through the nozzle B.   Here they meet

[1] Leffer, British Patent 19,051, Aug. 20, 1912; French Patent 439,476 (1912).

[2] U. S. Patent 1,134,677, April 6, 1915.

[3] J S. C. I. 1918, 760A; Chem. Abs. 1918, 1347 and 2686; 1919, 185; U. S. Patent 1,280,179, Oct. 1, 1918; British Patents 113,264, Nov. 16, 1917; Int. Conv. Feb. 2, 1917, and 119,441, Nov. 16, 1917.

hot combustion gases generated in the combustion chamber C. Both chambers A and C are in direct communication and are built to withstand a pressure of 600 pounds per square inch.

The products of reaction expand through valve D and then bubble up through a mass of fresh oil in the still E. This not only scrubs the products from the cracking chamber but also (since the oil in E is the oil which is submitted to the cracking in the chamber A) preheats the
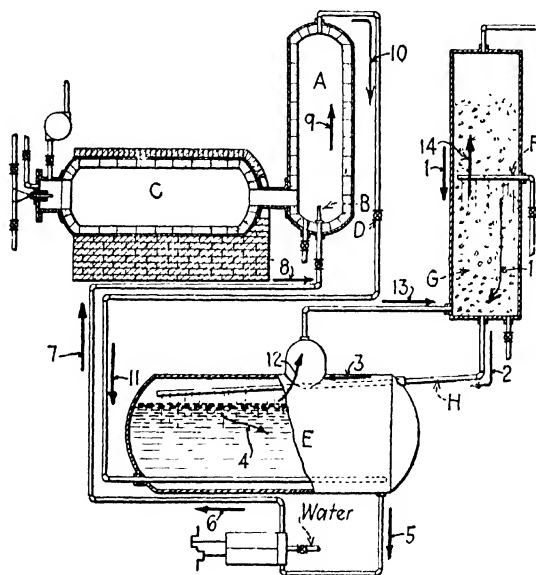
Fig. 159. — Apparatus for cracking oils in the presence of hot combustion gases, proposed by R. B. and D. T. Day.

charge. Distillation at the ordinary pressure takes place in still E. The vapors produced by this distillation together with the noncondensable gases from the cracking and combustion operations pass up through a scrubbing tower G where they are washed by a descending spray of fresh oil, admitted through the pipe F (Fig. 159). The temperature at the outlet end of the tower G is maintained at 190° C. (374° F.) so that materials condensing at this point or lower will be led back again to the oil still, and all vapors not condensed at this temperature will be led to a second condenser and condensed to obtain gasoline. The pipe F is the point where fresh oil is supplied to the system. The distillation and cracking of crude oil is particularly mentioned but apparently the apparatus is applicable to a variety of petroleum products, since the reaction temperature is stated to be capable of a

variation of from 355° C. (671° F.) to 1650° C. (3002° F.) and from atmospheric pressure up to a pressure of six hundred pounds per square inch.

The course taken by the oil in its passage through the apparatus is indicated in Fig. 159 by means of numbered arrows, starting at the fresh oil supply pipe *F*.

J. R. Rose [1] makes fuel gas by passing superheated steam and a hydrocarbon oil through a duct heated to at least 2200° F. (1200° C.) to induce dissociation. A heated mixture of liquid hydrocarbon and superheated or dried steam is then added, the final mixture passing through another duct also heated to at least 2200° F. (1200° C.). Carbon dioxide is then removed from the gaseous product.

Rose [2] injects a liquid or gaseous hydrocarbon into a generator by a stream of hydrogen under pressure; a liquid hydrocarbon of a different series is also introduced into the generator, and the mixture of the three fluids is subjected in the generator to the action of highly heated refractory material. The resulting gaseous fuel is freed from carbon, scrubbed, and then enriched by conducting it through liquid hydrocarbon oils.

Rose [3] also prepares gas containing as high as 98 per cent hydrogen by passing natural gas or oil over refractory surfaces heated to 1650° C. (3000° F.).

J. H. Yocum [4] obtains oil by the destructive distillation of wood in the presence of nascent hydrogen.

Sabatier [5] prepares water gas free from carbon dioxide and then passes the mixture in contact with heated nickel, to produce methane. The removal of carbon dioxide prevents carbonization of the nickel in the subsequent catalytic reduction. It is also important to use water gas of constant and suitable composition (a sufficient amount of hydrogen) for the same reason.

F. F. Schauer [6] uses a Lowe type water-gas machine and substitutes natural gas in it in place of steam. The effect is the deposition of carbon from the methane in the natural gas and the liberation of hydrogen.

A. R. Frank [7] produces hydrogen by purifying natural gas and then heating it to 1200° C. (2190° F.) or higher.

W. O. Snelling, [8] heats carbon compounds in a closed chamber or tube with walls more permeable by hydrogen than by other substances present, and the hydrogen formed is thus withdrawn during the reaction.

[1] J. S. C. I. 1918, 144A; .U. S. Patent 1,252,033, Jan. 1, 1918.
[2] J. S. C. I. 1917, 862; U. S. Patent 1,230,226, June 19, 1917.
[3] U. S. Patent 1,254,360, Jan. 22, 1918.
[4] Chem. Abs. 1918, 628; Canadian Patent 180,130, Oct. 30, 1917.
[5] U. S. Patent 956,734, May 3, 1910.
[6] Chem. Abs. 1912, 3511; Progressive Age, 30, 786-7.
[7] Chem. Abs. 1914, 3359; U. S. Patent 1,107,926, Aug. 18, 1919.
[8] J. S. C. I. 1915, 249; U. S. Patent 1,124,347, Jan. 12, 1915.

F. C. Ruff[1] arranges equipment to preheat petroleum oil in a pipe coil in a preheating furnace to a temperature somewhat below the cracking temperature and the oil is then led into a cracking chamber previously heated to a higher temperature by an internal gas burner. This cracking chamber is provided, on its interior, with iron catalytic members which may be in the form either of baffle plates or of bricks. Steam or a fixed gas such as hydrogen, methane or ethylene is also introduced into the cracking chamber to maintain such an equilibrium that formation of fixed gas from the oil itself is minimized. The steam or gas used for this purpose is preheated to about $600°$ to $870°$ C. and is injected into the cracking chamber at a point directly opposite to the point of ingress of the petroleum. If steam is employed, the high temperature may effect dissociation of the steam and combination of its hydrogen with unsaturated hydrocarbons present in the reaction zone. The gas supplied to the cracking chamber, however, is preferably a mixture of gases such as is obtained by the cracking of the oil undergoing treatment, as their use tends to minimize gasification of the oil itself. Such fixed gases may be re-used cyclicly in the process. In case the oil used is a fraction boiling up to $205°$ C., the operation is carried on but once and the conversion is completed at a temperature of $600°$ to $870°$ C., but if crude oil, residuum, or other products of higher boiling point are to be dealt with, the light oils obtained in the first treatment of these heavy oils should be subjected to a repetition of the process. In the first stage of this repeated operation the oil is thoroughly cracked and heavy asphaltic residuum is separated on the bottom of the cracking chamber. This residuum is suitable for the manufacture of coke. The temperature in the preheating coil is maintained at a point sufficiently low to prevent deposition of carbon in the coil. The process is reported capable of operation so as to obtain large yields of aromatic hydrocarbons.[2]

[1] Chem. Abs. 1920, 464; U. S. Patent 1,325,582, Dec. 23, 1919.

[2] Apparatus is described in U. S. Patent 1,319,420, Oct. 21, 1919.

CHAPTER XIX

CHEMICAL METHODS OF CRACKING OILS

The employment of aluminum chloride, aluminum alloys and amalgams of aluminum has led to many theoretically and practically important syntheses in organic chemistry. It was, however, recognized at an early date that the reaction is, even from a practical point of view, a reversible one.

Considering the reaction,

Benzene   Benzyl chloride   Diphenylmethane

$$\bigcirc + ClCH_2 \bigcirc + [AlCl_3] = \bigcirc CH_2 \bigcirc + HCl$$
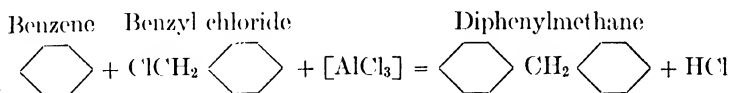
it appears, on theoretical grounds, by maintaining suitable concentrations and other conditions, to be possible to decompose diphenylmethane, by the use of hydrochloric acid and aluminum chloride, into benzene and benzyl chloride.

It is also conceivable that, in the presence of a sufficiently strong reducing agent, the benzyl chloride might be reduced to toluene, and that from diphenyl methane the ultimate products obtained might be benzene and toluene. An effect of this nature may be the basis of those methods that use metallic aluminum to decompose heavy petroleum oils into lighter ones in the presence of hydrochloric acid (gaseous). In this case the hydrochloric acid may be furnished by passing chlorine gas into the boiling oil, the chlorohydrocarbons formed possibly reacting in the presence of aluminum with hydrocarbons to form condensation products and the latter, in turn, breaking down under the influence of the dry hydrogen chloride (in the presence of aluminum), to form chlorohydrocarbons of lesser molecular weight, these in turn being reduced to the corresponding hydrocarbons by the action of the aluminum.

This is suggested as one of the possibilities. It is not definitely known just what is the mechanism of the oil cracking process involving the use of aluminum chloride or aluminum and chlorine.

One of the principles upon which is based chemical methods of decomposition of petroleum oils is the raising of the boiling point of oils by condensation and polymerization, so that cracking or decom-

posing temperatures may easily be obtained without much rise in pressure of the system under treatment. Aluminum chloride, ferric chloride, hydrochloric acid, phosphoric acid, sulphur, sulphur chloride, tin chloride, even sulphuric acid; in fact any reagent which will condense with, or polymerize hydrocarbons may be used for the purpose of securing high-boiling relatively unstable hydrocarbon products, as one of the steps toward the ultimate objective.

Friedel and **Crafts** (Abel)[1] treated petroleum with aluminum chloride (5–20 per cent) at temperatures from 100° to 600° C. (212°-1112° F.). The oil was thereby changed into light oils, gas, and heavy paraffin oils. Sulphur compounds were said to be simultaneously destroyed. Metallic oxides were also added. Naphthalene was converted by this method partly into benzene and toluene.

S. C. J. Olivier[2] has made a dynamic study of the condensation of p-bromobenzenesulphonic acid chloride with benzene and its derivatives in the presence of aluminium chloride.

It is stated that in carbon bisulphide solution no sulphone is formed as in benzene solution, but an aluminum complex, instead, according to the equation:

$$C_6H_4BrSO_2Cl, AlCl_3 + C_6H_6 = C_6H_4BrSO_2, AlCl_2 + C_6H_5Cl + HCl.$$

As this reaction takes place (in absence of carbon bisulphide) in solutions to which traces of sulphur chloride (S_2Cl_2) are added, and more rapidly in carbon bisulphide solutions which have been kept, than in fresh solutions, it is said to be probable that the reaction is due to sulphur chloride, which retards the formation of sulphone. When aluminium bromide is used instead of the chloride a pale yellow, hygroscopic, crystalline aluminium complex compound, $C_6H_4BrSO_2$, $AlBr_2$ (decomposing at 125°–132° C), is formed with liberation of free bromine. Study of the formation of sulphone in solutions with benzene or its derivatives shows that the sulphonic acid chloride reacts only as an equimolecular compound, $C_6H_4BrSO_2Cl$, $AlCl_4$; one molecule of aluminium chloride can convert only one molecule of sulphonic acid chloride, the constant of the reaction (when excess of aluminium chloride is not present) being proportional to the concentration of aluminium chloride; when excess of aluminium chloride is present the constant increases greatly. The velocity of reaction using the benzene derivatives named diminishes in the order — toluene, benzene, chlorbenzene, brombenzene, nitrobenzene. These facts are interpreted by assuming that the acid chloride is activated in the compound, $C_6H_4BrSO_2Cl$, $AlCl_3$, while the benzene is activated in proportion to the amount of aluminium chloride combined with the sulphonic acid or sulphone. Free aluminium chloride is stated to be a most energetic catalyst.

Steele[3] has undertaken experiments to elucidate the mechanism of the aluminum chloride condensation reactions. After giving a

[1] J. S. C. I. 1878, 411; British Patent 4769, Dec. 15, 1877.

[2] J. S. C. I. 1915, 217; Rec. Trav. Chim. Pays-Bas, 1914 [33], 91–182; Bull. Soc. Chim. 1914 [15], 783–784.

[3] Journ. Chem. Soc. Transactions, 1903, 1470.

resumé of other endeavors along the same line, [1] he states that for the
synthesis of hydrocarbons no satisfactory explanation has been hitherto
advanced. If the ketone synthesis (see Perrier, *loc. cit.*, below) is
conditioned by the occurrence of intermediate compounds which can
be easily isolated, the fact that the isolation of similar compounds in
other cases is difficult or impossible is no evidence of their nonexistence,
and it is probable that the formation of such compounds is a necessary
condition of the Friedel-Crafts reaction.

Aluminium chloride as a condensing agent usually behaves, it is
said, in such a way that there is a definite relationship between the
amount of substance formed and the amount of chloride used. In
some instances, a large quantity of the latter is required to bring about
condensation, and in others the quantity is so small that the reaction
partakes of the nature of catalysis, and the latter condition seems, it
is stated, to obtain more generally when ferric chloride is employed.

This apparently fundamental difference of behavior is probably
dependent on and explained by the formation, or nonformation, of
a compound of the aluminium (or ferric) chloride with the product
of the reaction, and on the stability or degree of dissociation of this
compound.

Two extreme cases may be considered:

(1) The compound of aluminum chloride and final product is perfectly stable
or non-dissociable, (2) complete dissociation takes place, or no compound at all is
formed. In the former case, if the compound is assumed to be one in which the
two components are present in equivalent proportions, then, it is said, every gram-
equivalent of reagent (acid chloride, for example) would, in the presence of an ex-
cess of the second reacting substance, require approximately quantitative reaction.
In the second case, where complete dissociation occurs, the metallic chloride should
behave as a true catalyst, since it would be constantly regenerated, and the
quantity present would influence only the velocity of the reaction. In intermediate
cases, where the final compound with metallic chloride may be partially dissoci-
ated, it must necessarily follow that the greater the extent of this dissociation the
less chloride will be required to bring about reaction between a given quantity of
reacting substances.

Freidel and Crafts have shown that, besides the synthetical, there is also a
disruptive action induced by aluminium chloride, as, for instance, the decomposi-
tion of toluene into benzene and methyl chloride in the presence of an excess of
hydrogen chloride, and it is probable that many more of these reactions are re-
versible, a fact which, if recognized, would go far to explain not only the poor
yields, but also the extremely complicated and unexpected compounds which are
sometimes obtained.

[1] **Perrier,** Ber. 1900, 815; **Boesken,** Rec Trav. Chim 1900, 19; **Kronberg,**
J. Prak Chem. 1900 [2], 61,494; **Kohler,** Amer. Chem. J. 1900, 385; **Gustavson,**
Chem. Centr. 1883, 344; **Coombes,** Compt rend. 1886, 103,814; **Konowaloff** and
Plotnikeff, J. Russ. Phys. Chem. Soc. 1899, 31, 1020; **Nencki,** Ber. 1899, 32,
2414; **Gurewitch,** J. Russ. Phys. Chem. Soc. 1902, 34, 625.

Perrier [1] reviews his earlier work in the preparation of double compounds 'of organic bodies with metallic chlorides. In the preparation of ketones by the aluminum chloride method [2] he has shown that the reaction takes place in the two following steps:

(1) $2R.CO.Cl + Al_2Cl_6 = (R.CO.Cl)_2 Al_2Cl_6$

(2) $(R.CO.Cl)_2 Al_2Cl_6 + 2C_mH_n = 2HCl + 2(R.CO.C_mH_{n-1}).Al_2Cl_6.$
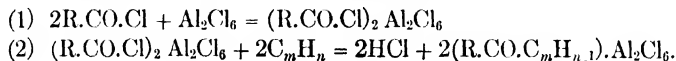
This hypothesis which he was able to substantiate by the isolation of double compounds of aluminum chloride and acid chlorides and by the reaction of these bodies with hydrocarbons enabled him to modify the Friedel-Crafts reaction in the following manner:

First the double compound $(R.CO.Cl)_2 Al_2Cl_6$ is prepared by gentle heating of equimolecular quantities of acid chloride and aluminum chloride. This is dissolved in carbon bisulphide and reacted upon by the corresponding quantity of hydrocarbon. The double compound of aluminum chloride and ketone then precipitates in a crystalline form which upon treatment with water is decomposed and yields the ketone. This method is stated to give better yields than the ordinary method.

Pictet and **Lerczynska** [3] find that anhydrous aluminum chloride dissolves in the higher fractions (boiling point above 150° C.) from petroleum to a brown solution, which on distillation yields as first fraction (boiling point 40°–140° C.) a product possessing all the properties of light petroleum spirit (benzine). Ten per cent of the weight of the petroleum is given as a suitable amount of aluminum chloride to use. The yield of petroleum spirit is said to depend only on the source of the petroleum and not on the rate of distillation or pressure, and the product is not altered by a further treatment with aluminum chloride. Calcium, zinc, chromium, copper, mercuric, and silicon chlorides are stated to be without action on petroleum; ferrous and ferric chloride have an incomplete action at a higher temperature. The petroleum spirit produced by the action of aluminum chloride is a colorless, nonfluorescent liquid (specific gravity 0.72) with a pleasant ethereal odor; it consists of *saturated* hydrocarbons, and is said to be free from chlorine and sulphur.

Concerning the decomposition of polyalkylbenzenes, **E. Boedtker** and **O. M. Halse** [4] state that a reversal of the Friedel-Crafts reaction can in general be brought about with more or less facility by the action of aluminium chloride on the alkylbenzene in presence of a large excess of benzene. In the case of the xylenes alone this re-

[1] Ber. 1900, 815.

[2] Compt. rend. 116, 1300, and Inaugural Thesis of the Faculty of Science of Paris, 1896, 21.

[3] J. S. C. I. 1916, 1098; Bull. Soc. Chim. 1916, 19, 323–334.

[4] J. S. C. I. 1917 (36), 129; Bull. Soc. Chim. 1916 (19), 444–449.

action does not succeed, but when polyethyl-, isopropyl-, butyl-, and amylbenzenes were boiled with aluminium chloride in presence of ten times their weight of benzene, quantities of the monoalkyl-benzene, varying in each were formed according to the scheme:

$$C_6H_4 (C_2H_5)_2 + C_6H_6 = 2C_6H_5 (C_2H_5)[1]$$
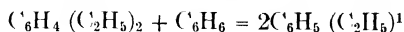
Of the greatest interest, however, was the formation in excellent yield of toluene and cumene from cymene, which is available in large quantities as a by-product of the sulphite-cellulose process. Ninety grams of cymene in 900 grams of benzene gave, on boiling for 10 hours with 4.5 grams of aluminium chloride, a yield of 44 grams of toluene and 68 grams of cumene, corresponding to 80 per cent of that theoretically possible, leaving a residue of only 3-4 grams of gummy material. It is said that the polyhalogen derivatives of benzene could not be decomposed by the action of aluminium chloride and benzene in this manner.

The work of **Huston** and **Friedemann**[2] would indicate that a hydroxyl group is capable of acting in a manner similar to that of a chlorine atom (substituted or contained in an organic body) in aluminum chloride syntheses.[3]

Ipatiev and **Rutula**[4] have investigated the polymerization of ethylene by means of the chlorides of zinc and aluminum. Ethylene under 70 atmospheres pressure and 270° C. (518° F.) in the presence of zinc chloride yields a liquid polymer. Forty-one per cent of this polymer boiled below 300° C. (572° F.). It consisted of olefins, paraffins and naphthenes. The high boiling fractions contained more olefins than saturated compounds. The saturated compounds were made up of both paraffins and naphthenes. The fractions boiling below 145° C. contained on an average 28 per cent of olefins.

When aluminum chloride is substituted for zinc chloride in the

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[1] This shows the interesting phenomenon of the transfer, or migration of an alkyl radicle from one molecule to another

[2] J S C I. 1917, 2 5A; J Amer Chem. Soc. 1916 [38], 2527–2533.

[3] They have shown that among the products of the interaction of benzyl alcohol, benzene, and aluminium chloride are diphenylmethane, produced in largest amount and smaller compounds of p- and o-dibenzylbenzene, a compound $C_{27}H_{24}$, boiling point 308°–316° C at 20 mm, which is probably a tribenzylbenzene or methylene-bisdiphenylmethane, and anthracene. The yields of these products are greatly influenced by the proportions of the reagents used, an excess of benzene favoring diphenylmethane formation Similar products were obtained from benzyl ethyl ether, benzene, and aluminium chloride, and from chloromethyl ethyl ether, benzene, and aluminium chloride. In the latter case formaldehyde is, it is said, probably an intermediate product.

[4] Ber. 1913, 1748.

polymerization of ethylene, the reaction is much more violent. Under conditions similar to those used with zinc chloride, aluminum chloride is said to yield only coke and gas.

Liquid products are obtained at the ordinary temperature with aluminum chloride. These consist of saturated and unsaturated hydrocarbons, the saturated bodies being mostly paraffins.

The reaction between benzene, aluminum and mercuric chloride has been studied by **W. Gulewitsch** [1] who observes that if a mixture of 10 grams (1 mol.) of aluminum turnings and 151 grams ($1\frac{1}{2}$ mols.) of mercuric chloride, be covered with 15 grams of benzene, the mass becomes heated and the benzene boils. The reaction is allowed to continue and another 43 grams benzene (2 mols. in all) are added. Hydrogen chloride is evolved and a reddish-brown layer of liquid is produced, from which crystals were isolated having the composition C_6H_6. $AlCl_3$. $HgCl$.

R. H. Brownlee [2] utilizes the polymerizing power of aluminum chloride to convert unsaturated petroleum distillates into lubricating stock. The distillates are heated and agitated with aluminum chloride, light oils distilled off, the residue washed, transferred to a still and reduced with fire and steam to make lubricating oils of the desired viscosity.

The apparatus shown in Fig. 160 is used.

A is a cylindrical vessel in the center of which is a rotatable shaft having a series of agitating paddles or beaters. The shaft is supported in a step box having surrounding clearance for circulation and passes upwardly through a stuffing box and a top bearing, and is rotated. The vessel A is surrounded by a hot water or steam heating coil, and a valve and conduit provide for withdrawal of accumulated contents from the bottom of the vessel.

Petroleum distillate containing a considerable percentage of unsaturated hydrocarbons is first treated with sulphuric acid in the usual manner to remove any objectionable matter, and is then charged into vessel A through a manhole B.

About one tenth of a pound of anhydrous aluminum chloride per gallon of distillate is added. The vessel is then closed and the stirring paddles are actuated, operating to agitate the liquid upwardly and the temperature is raised to from 300° to 400° F. (149°–204° C). The desired reaction will take place, it is said, to some extent at ordinary temperatures, but slowly and incompletely, compared to the higher temperatures noted. After stirring, for say an hour to an hour and one half, the stirring is stopped and a heavy dark colored sludge, resulting from the operations, is allowed to settle to the bottom of vessel A and is drawn off through valve D.

Any light naphtha vapor in the vessel, i.e., saturated hydrocarbons not exceeding say 5 per cent to 10 per cent of the total charge, may be drawn off, and condensed. This product has an acid reaction and may be easily neutralized with

[1] J. S. C. I. 1904, 627; Ber. 1904 (37), 1560–64.

[2] U. S. Patent 1,309,432, July 8, 1919.

soda. It is passed through a washer to remove excess of soda and then drawn off and used as a fuel for engines.

The contents of agitating vessel A are cooled and again stirred, and are then allowed to stand, when coloring substances will settle to the bottom of the agitator and are drawn off Soda or caustic soda solution is then added. The contents of the agitating vessel are again stirred and allowed to settle to the bottom. Excess of alkaline material is washed out with water and is drawn off At this stage in the process, it is noted, the remaining product will have become clear and of a light amber color, and is drawn off to be treated with steam in a still In steam distilling the product, at first a certain proportion of naphtha vapor is produced. If all of the distillates from the still having a flash point higher than about 300° F. (149° C.) are mixed, an excellent light lubricating oil is said to be obtained, of low viscosity. If desired, also, the product may be divided as taken off, into separate fractional quantities of lubricating distillates, thereby obtaining a number of oils having different gravities and viscosities.

It is stated that the distillate from this oil has a low cold test, -60° to -70° F. and will remain bright below those temperatures.

The oil remaining in the still will now have been reduced to the desired flash and viscosity and may be filtered to improve the color and clarity.
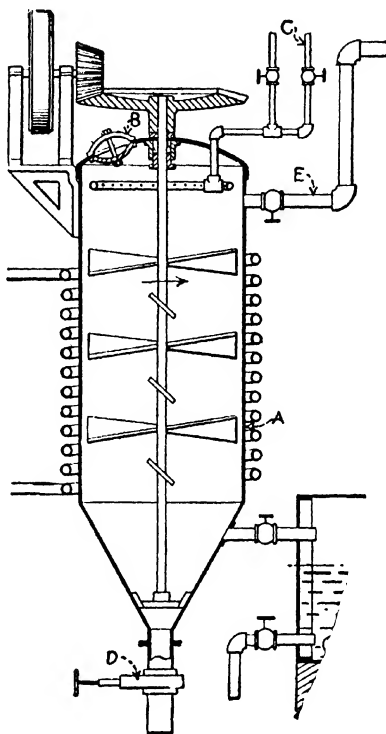
Fig. 160. — Apparatus employed in manufacturing lubricating stock by means of aluminum chloride, according to R. H. Brownlee.

The **Chem. Fabrik Auf Actien** [1] make condensation products from unsaturated hydrocarbons by allowing anhydrous inorganic chlorides, as catalyzers, to act upon mixtures of paraffin hydrocarbons with hydrocarbons poorer in hydrogen which contain at least two double bonds. The reaction products of a previous run can be employed also as catalyzers.

The **All-Gemeine Ges. Chem. Ind.** [2] (Justice) frees cracked mineral

[1] Chem. Abs. 1915, 1096; German Patent 278,486, May 24, 1913.

[2] J. S. C. I. 1915, 1004; Chem Abs. 1916, 116; English Patent 3572, Feb. 11, 1914.

oils from malodorous and resinifying substances by treatment with a salt of a heavy metal having a condensing action, such as the chlorides of tin, zinc, iron and copper, and then distilling. The residue left in the still is a viscid product which ultimately solidifies to a glass-like mass.

Dunstan [1] removes olefins and diolefins, which impart a yellow color and objectionable odor to petroleum cracked by the usual methods by slowly distilling the cracked oil in the presence of about one per cent of an anhydrous chloride (e.g., anhydrous aluminum chloride). To render it more effective, the chloride may be applied dissolved in an anhydrous solvent (e.g., absolute alcohol), or mixed with a dry inert material; the mixture is stirred during distillation.

Heusler [2] in working with distillates from lignite tar has observed the presence of considerable quantities of thiophene and that the chlorides of titanium, iron and aluminum act readily on thiophene.

The unsaturated substances in coal tar distillates like coumaron and indene are said to be polymerized by much smaller amounts of aluminum chloride than are the unsaturated hydrocarbons in lignite and shale tar. Fractions of lignite tar boiling below 200° C. (392° F.) were treated with aluminum chloride, only 5 per cent of the reagent being necessary to completely remove olefins, thiophene and its homologues. By decomposing the aluminum complexes with lime and then distilling off the resulting oils, considerable quantities of high boiling oils were obtained.

Alsace petroleum oils boiling between 130° C. (266° F.) and 170°C. (338° F.) yield 93.5 per cent of saturated hydrocarbons, it is said, by boiling with 2 per cent of aluminum chloride and separating the small resinous mass which forms. On treating a fraction of Ohio petroleum with aluminum chloride, a lively evolution of hydrogen sulphide is obtained. High boiling oils are not formed in this case, so it is concluded that this fraction does not contain any considerable amount of unsaturated hydrocarbons. This treatment removes sulphur compounds. The illuminating oil fraction of Ohio oil heated with 0.8 per cent aluminum chloride to incipient boiling yields 97 per cent of pure free oil, which gives only a reddish coloration with sulphuric acid.

The oils obtained by **Engler** [3] in distilling fish oil under pressure, in part boiled between 100° and 120° C. (212°–248° F.) and contained a considerable amount of unsaturated hydrocarbons. This fraction was treated with aluminum chloride and the unattacked oils distilled off (using steam). The amount of unattacked hydrocarbons found by this

[1] J. S. C. I. 1918, 727A; English Patent 119,751, Nov. 28, 1917.
[2] Zeitschr. Angew. Chemie, 1896 [9], 288 and 318.
[3] Ber. 1888 (21), 1816; 1889 (22), 592; 1893 (26), 1436.

method agreed closely with the figures reported by Engler when employing a different method of determination. This showed that it was the unsaturated oils which the aluminum chloride had polymerized into high boiling viscous oils.

Adiassewitch [1] treated the unsaturated burning oils derived from shale, with aluminum chloride, observed the evolution of hydrochloric acid and noted that by distilling the reaction product, refined burning oils were obtained leaving a residue suitable as lubricating stock.

The treatment of the burning oil was carried out as follows:

Into a wrought iron cylinder, lined with lead and provided with an agitator and a steam coil, is introduced dilute sulphuric acid of 60 per cent strength amounting to about 0.75 per cent of the oil, which is next introduced into the vessel. Pressure is then applied by means of an air pump at about 15–20 lbs. per square inch. Steam is passed through the coil until the temperature is between 40° and 50° C., at which temperature the oil is kept for about ½ hour, the stirrer being at work meanwhile. The oil is now allowed to rest until the acid and other matters have settled and then separated, and may then be at once washed with water or may be agitated again with diluted sulphuric acid without heat and pressure. The oil is next transferred to another vessel which may be a cylinder not lined with lead but otherwise is similar to the first one; here it receives an addition of about 0.3 per cent of its weight of caustic soda dissolved in water, preferably to form a lye of 1 320 specific gravity. The lye is added gradually while the stirrer is rapidly rotated and the temperature is raised by the steam coil. A pressure of about 25 to 30 lbs per square inch is applied and the temperature is maintained at near the boiling point of the oil until the mixture is completely emulsified. The agitation is now stopped and to promote settlement the vessel is attached to a reflux condenser and open steam blown through the oil for a short time. The caustic soda liquor and tar is then drained off, the oil washed with water and transferred to a settling tank where it must be allowed to become thoroughly dry, this being aided if necessary, by heating with closed steam.

The dry oil is next pumped into an iron vessel having a stirrer and a reflux condenser the outlet end of which is connected with apparatus for absorbing hydrogen chloride and is provided with a valve The oil is heated and stirred while there is introduced aluminium chloride amounting to about 2 per cent of the weight of the oil. The chloride may be introduced either in the gaseous or solid state; in the latter case a valve which will allow introduction without access of moisture to the aluminium chloride is advantageous. In the former case the aluminium chloride may be heated in a retort connected with the vessel. After the aluminium chloride has been added the temperature of the oil is raised by closed steam or direct heating to about 150° C. and maintained at this degree for about 3 hours. At the same time the valve on the reflux condenser is closed by degrees to raise the pressure to 10-12 lbs. per square inch, but is afterwards opened at intervals to allow gases to escape. At the end of the operation the oil is allowed to settle and then transferred to another vessel, washed with water containing a little lime and finally distilled to separate the burning oil from the lubricating oil; the distillate being refined in any known manner.

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[1] British Patent 4431, Feb. 25, 1903.

Fig. 161 shows a longitudinal vertical section through part of a cylinder having a valve suitable for the introduction of aluminium chloride. The cylinder a has a stirrer b and a hopper c, which has an air-tight cover d. Within the hopper are two grinding rollers and just below these is a slide valve f. The aluminium chloride is charged into the hopper which is then covered. The rollers are rotated and the valve f opened, whereupon the aluminium chloride passes slowly into the cylinder. By connecting with the cylinder a heated retort containing aluminium chloride, the latter can be introduced in the state of vapor.

For a heavy oil the sulphuric acid treatment may be conducted at a temperature as high as 150° C. and a pressure of about 40 lbs. per square inch and the proportion of diluted acid may be 0.5 to 5 per cent. Similarly the pressure may be increased to 50 lbs. per square inch, in the caustic soda treatment and to 30 lbs. per square inch in the treatment with aluminium chloride. The proportion of the latter may vary according as the proportion of sulphur in the oil is low or high. The

Fig. 161. — Apparatus used in treating oils with aluminum chloride by the method of Adiassewitch.

temperature of heating with aluminium chloride may also be higher than that given if the oil be of higher boiling point.

Henderson and **Gangloff** [1] have carried out a large number of admirable experiments on the action of aluminum chloride upon unsaturated compounds. They note that on shaking ordinary gasoline with anhydrous chloride, the unsaturated hydrocarbons are converted into a dark colored sludge, and the resulting gasoline gives no color with concentrated sulphuric acid. Petroleum ether acts in a similar way. These investigators have prepared a large number of addition compounds of aluminum chloride and unsaturated compounds, the chief results of this work, so far as it may have a bearing in the gasoline field, being cited below:

1. *Action on Acetylene and Ethylene.* Dry acetylene prepared from the carbide was passed into a closed vessel containing finely powdered freshly prepared anhydrous aluminum chloride. No noticeable absorption occurred within several hours. Upon heating the aluminum chloride to 60°–62° C. a reddish brown sublimate appeared, dense vapors were produced and the sublimate soon turned black

[1] J. Am. Chem. Soc. 1916, 1382 and 1917, 1420.

and remained unchanged, after heating to 140° C. Heating to 240° C. yielded nothing but tar. The black substance resembled pitch and showed no crystalline form. It was evidently a complex mixture. Dry acetylene was then passed into a solution of aluminum chloride in absolute alcohol and the solution was kept saturated with acetylene. After five days, small, colorless, glistening crystals appeared. Analysis clearly indicated that the product had the formula $AlCl_3.2C_2H_2.2H_2O$. The corresponding compound prepared from ethylene had the formula $AlCl_3.3C_2H_4 H_2O$.

2. *Action on γ-Butylene*, $(CH_3)_2C:CH_2$. Methyl alcohol was used as solvent for the aluminum chloride. The product obtained has the formula: $AlCl_3((CH_3)_2C = CH_2.2CH_3OH.H_2O$.

3. *Action on Amylene*, $(CH_3)_2C:CH.CH_3$. Boiling point 36°–38° C. Dry powdered aluminum chloride reacted at once with the pure liquid giving a series of bright colored tars, yellow to red to sienna as the amount of chloride added was increased. These tars, when dissolved in methyl or ethyl alcohol yielded on fractionation, a series of carbinols (alcohols) as verified by the Baumann-Schotten reaction. Trimethyl carbinol $((CH_3)_3COH)$ (tertiary isobutyl alcohol) was formed in largest amount; on further heating some decylene was obtained as a heavy dark fluorescent oil. A solution of aluminum chloride in absolute ethyl alcohol mixed with amylene gave a fairly well crystallized product within two weeks. This has the formula:

$$AlCl_3 \cdot C_5H_{10} \cdot CH_3OH.$$

4. *Action on Phenyl Ethylene*, $C_6H_5CH:CH_2$. Two products were secured; one has the composition $AlCl_3 \cdot C_6H_5CH:CH_2$. A specimen of this well crystallized body, on standing several months, altered its composition, took up water, became oily and was converted into a body with the formula:

$$AlCl_3 \cdot 2C_6H_5 \cdot CH:CH_2 \cdot 2H_2O.$$
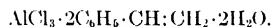
The investigators also undertook experiments to test the value of different anhydrous chlorides in condensing reactions. In the preparation of benzophenone from benzoyl chloride and benzene, aluminium chloride was found to be the most efficient, giving yields of 70–71 per cent. Under the same conditions with reactions carried out simultaneously, ferric chloride gave yields of 60–62 per cent; zinc chloride 28–32 per cent but chromic chloride gave no yield. Chromic chloride does not appear to act as a condensing agent but resembles more closely some of the rare earth chlorides, e.g., those of lanthanum. Cuprous chloride also failed to effect condensation. These results along with the low yields obtained with anhydrous zinc chloride make it appear that some of these anhydrous chlorides are specific in their action.[1]

[1] No crystalline product suitable for analysis was obtained with cyclohexene. The addition of the dry chloride to oleic acid resulted in the immediate formation of heavy tars. On standing, these tars became hard like asphalt. Aluminum chloride dissolved in methyl alcohol and mixed with oleic acid in equimolecular amounts, gave in four months a crystalline mass resembling brown sugar. The product has the formula: $AlCl_3 \cdot C_{17}H_{33} \cdot COOH$ In this case the effect of the increased number of

It is stated that **Menschutkin**,[1] working with the anhydrous chlorides of iron, antimony, arsenic, tin, etc., found similar results. Henderson and Gangloff further state that owing to the higher temperature conditions involved in the process of oil cracking, it is not likely that the compounds that they obtained are the ones formed in that process, but that it is only reasonable to assume the formation of similar combinations between the metallic chlorides and other unsaturated bodies present. These chemists believe that there appears to be little doubt that in the catalytic (aluminum chloride) oil cracking processes, the catalyst combines with certain products in the reaction so that the unsaturated portion of the oil is held back from the distillate.

Egloff and **Moore** [2] have studied the effect of the catalytic or chemical action of the chlorides of metals and non metals upon the formation of gasoline from a paraffin base kerosene.

The experiments were carried out in an 800 c.c. Kjeldahl flask fitted with a two-holed stopper, through one hole of which was attached a Glinsky distilling head connected with a Liebig condenser. Through the other hole a glass tube extended to the bottom of the flask; hydrogen chloride and chlorine were passed through this tube, and reacted with the metals and non metals in the flask. A charge of 400 or 500 c.c. of kerosene and 10 per cent by weight of the catalyst was placed in the flask, and the mixture distilled with a Bunsen burner over an average period of three hours. The appearance of the distillates from the different runs varied widely, as did the residues in the flask. One hundred c.c. of the distillate were redistilled in an Engler flask, and the fraction up to 150° C. (302° F.) was taken as gasoline. In the chlorine runs on phosphorus and sulphur the action was so strongly exothermic that flashes of light were emitted under the oil. The following results were obtained:

carbon atoms is noteworthy. Again no water or alcohol of crystallization appears necessary for a crystalline product, similarly to the case of phenyl ethylene. The product obtained with fumaric acid had the formula, $AlCl_3 \cdot C_4H_4O_4$. The dry chloride acting on a sample of furfuraldehyde gave a heavy black tar at once with evolution of sweet odors. A solution of aluminum chloride in methyl alcohol reacted slowly with the furfuraldehyde forming a well crystallized, shiny, coal-black product in from five to eight days. The formula of the compound is: $AlCl_3 \cdot C_5H_4O_2 \cdot CH_3OH$. Benzaldehyde was dissolved in methyl alcohol and treated with aluminum chloride. A product was obtained which had the formula $AlCl_3 \cdot C_6H_5CHO \cdot CH_3OH$. The formula of the product obtained from allyl alcohol out of methyl alcohol solution was: $AlCl_3 \cdot C_6H_6O \cdot CH_3OH$. Anhydrous ferric chloride was now substituted for aluminum chloride. In all cases the reactions were very similar to those of aluminum chloride but less vigorous and not so complete. With amylene the compound formed had the formula: $FeCl_7 \cdot C_5H_{10} \cdot CH_3OH$ and on furfuraldehyde a product was obtained with the formula: $FeCl_7 \cdot C_5H_4O_2 \cdot CH_3OH$.

[1] (J. Russ. Phys. Chem. Soc. (1909) 41, 1089; (1911) 43, 1329.)

[2] Chem. Abs. 1916, 2399; J. S. C. I. 1916, 882; Met. Chem. Eng. 1916 [15] 67-9,

Table showing Comparative Action of Various Metals and Non-metals in Presence of Hydrogen Chloride and Chlorine, respectively

Using hydrogen chloride

	Magnesium	Selenium	Zinc	Sodium	Aluminum
Per cent recovered oil	75.1	45.0	70.0	70.0	71.0
Per cent gasoline	1.1	1.8	4.9	5.3	37.3

Using Chlorine

	Magnesium	Selenium	Zinc	Sodium	Aluminum	Phosphorus	Sulphur	Silicon
Per cent recovered oil.	67.5	48 0	.	.	73.8	55 0	67.5	60 0
Per cent gasoline.....	0.3	5.3	..	.	15.9	1.7	0.7	0.6

The following reactions are given to illustrate the addition and splitting off of the hydrocarbons. The paraffin hydrocarbons in kerosene are those with boiling points around decane, undecane, tridecane, and compounds of higher molecular weight. Their hypothetical reactions with aluminum chloride are set forth as follows:

$$AlCl_3 + C_{10}H_{22} + C_{11}H_{24} = C_{10}H_{22} \cdot AlCl_3 \cdot C_{11}H_{24}$$
$$= C_6H_{14} + C_{15}H_{32} + AlCl_3.$$
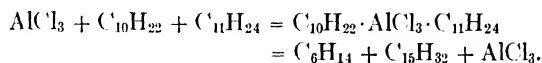
When hydrogen chloride was passed over aluminum, no unsaturated compounds were found in the gasoline fraction, but when chlorine was passed over the same metal, unsaturated hydrocarbons were found. The following hypothetical reaction is given to explain this result:

$$AlCl_3 + C_{10}H_{22} = AlCl_3 \cdot C_{10}H_{22} = C_5H_{10} + C_5H_{12} + AlCl_3.$$
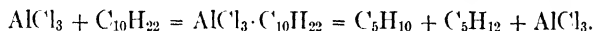
It is noted that hydrogen chloride gave a much better yield than the chlorine.

Moore and **Egloff** [1] give specific evidence concerning the comparatively large number of definite compounds formed by the action of aluminum chloride on benzene, toluene and xylene. They observe the formation of hexahydrotoluene from the action of aluminum chloride on toluene and xylene, respectively.

Egloff and **Moore** [2] summarize the results of their study of the action of aluminum chloride on fractions of a naphthene base oil as follows:

1. A naphthene base oil was subjected to fractionation of approximately 28 per cent of the total in six distillation cuts. These were distilled in 25° C. cuts and their physical constants determined. They

[1] Met. and Chem Eng. 1917 (17), 61. A review of the literature concerning the action of aluminum chloride on aromatic compounds is also given.

[2] Met. and Chem. Eng. 1916 (15), 340.

were then analyzed for the percentage of unsaturated, percentage of nitratable hydrocarbons, and the specific gravity and refractive index of the hydrocarbons unattacked by sulphuric and nitric acid were determined.

2. The six oils after treatment with aluminium chloride gave from 24.3 to 60.2 per cent yield of hydrocarbons boiling below the lowest boiling point constituent of the starting oil. The maximum conversion was in the highest boiling point oil.

3. The percentage of oil recovered after aluminium chloride treatment ranged between 60 and 79.3 per cent, the balance of the oil going to gas, carbon and losses due to neutralizing, washing and drying.

4. The specific gravity and the refractive index of the recovered oil was in each case lower than the starting oil, the greatest change taking place in the highest boiling fraction. This oil before treatment gave a specific gravity of 0.849; after conversion 0.774. A similar drop is to be noted in the refractive index of the oil.

5. The specific gravity and refractive index of the distillation cuts of the converted oils decrease as the boiling points of the starting oils increase.

6. The percentage of gasoline in the recovered oil ranged between 23.5 and 47.3 per cent. The gasoline formed was water-white, faintly aromatic and contained practically no unsaturated hydrocarbons.

7. The maximum percentage of gasoline on the basis of 100 gal. of oil used was found in the highest boiling point oil used and gave 32.1 per cent. The formation of gasoline from the six oils ranged between 18.4 and 32.1 per cent on basis of oil used for production. The highest percentage of gasoline converted from the highest boiling point starting oil gave the lowest specific gravity of 0.726. The specific gravity of the other gasoline cuts ranged between 0.726 and 0.801.

8. The formation of toluene and xylene reached a maximum in the recovered oil from the lowest boiling point starting oil, while benzene reached a maximum in the second lowest boiling point starting oil. These maxima were as follows on the basis of oil used for production; for benzene 1.11, for toluene 2.35 and xylene 7.80 per cent.

9. The percentage of unsaturated hydrocarbons in the oils before treatment was usually higher for the same distillation cut than in the converted oils. The maximum unsaturation in any distillation cut of the starting oils was 8.3 per cent while 10 per cent was the maximum in any distillation cut after conversion.

10. The percentage of nitratable hydrocarbons in the distillation cuts after conversion by aluminium chloride decreases as the boiling points of the starting oils increase. The percentage nitratable in the

distillation cuts gave values ranging between 0 and 43.6 per cent. These values were lower than any similar distillation cut before conversion. The high percentages of the nitratable hydrocarbons in the original oils is impressive, the distillation cut between 150° and 175° C. giving a value of 54.9 per cent.

11. The percentage of the stable hydrocarbons remaining after sulphonation and nitration in every case was greater in the converted oil.

The application of aluminum and chlorine in increasing the yield of naphtha has received thorough study in the hands of **McAfee.** That part of the work dealing with the application of aluminum chloride as such is described as follows: [1]

In the practical operation of this process, crude petroleum of any kind is first distilled until the naturally occurring gasoline and kerosene, if there be any present, is distilled off. In many crude oils and especially some of those from Texas, California and Mexico, there is substantially no gasoline present and very little kerosene. But in any event, the crude is first heated to free it of any moisture which it may contain, since the oil must be perfectly dry before adding the aluminum chloride. The next step is to add anhydrous aluminum chloride to the remaining residual oil, and then bring the mixture to boiling in the still. Boiling is usually around 500° F. and generally remains between 500° and 550° F. during the entire distillation, extending over a period of twenty-four to forty-eight hours. There is no need of employing extra pressure or vacuum or special still; any still with a stirrer in it suffices.

Granted sufficient time, the success or failure of this process depends upon the proper control of the temperature at which the oil vapors are allowed to leave the distilling system to enter the final condenser. Between the still and the final condenser are placed two air cooled condensers connected in series, which separate the low boiling oils from the high boiling oils, returning the latter together with any volatilized aluminum chloride to the still. For a 1000 barrel still, air condensers in the shape of drums of oval cross-section, 3' × 6' × 6' high may be used. In addition to the air condensers, a 3-foot dome is attached to the top of the still which serves to return most of the volatilized aluminum chloride and its compounds. The operation is so controlled that the vapor is kept at the desired temperature as indicated by a thermometer placed in the vapor line at the point of exit of vapor into the final or water cooled condenser. The temperature at this point should not exceed 350° F., otherwise not only will heavy oils distill over, but the aluminum chloride (or its compounds with hydrocarbons)

[1] **McAfee,** Trans. Am. Institute of Chem. Engineers, 1915 (8), 179–195.

will enter the condenser and clog it up. Under the first named condition, the distillate obtained will be a mixture of gasoline, solvent oil and kerosene which are afterwards separated by fractional distillation. These products are stated to be *all water white, sweet smelling, saturated and need no refining with sulphuric acid. In practice, no treatment is given them, except a washing with alkali, followed with water, to remove hydrogen sulphide.* With proper back-trapping of high boiling oils into the still from the air cooled condensers and a temperature of 300° F. in the vapor line, the distillate obtained will be gasoline alone, which is ready for the market when washed with an alkaline solution.

It is a mistake, it is observed, to assume that with a given amount of aluminum chloride and boiling it up with oil, the desired results will be obtained. The belief is expressed that the chemical action is one of association or combination in the liquid phase and dissociation in the vapor phase. It is well known that aluminum chloride exists in the solid and liquid states as Al_2Cl_6 and in the vapor state as $AlCl_3$. It is also well known with what avidity aluminum chloride in the solid or liquid state will combine with other salts to form double salts. The most common of these double salts is that of aluminum and sodium chloride. Aluminum chloride probably combines, it is stated, with these high boiling, complex hydrocarbons in much the same way as it combines with sodium chloride and when the boiling temperature is reached these double compounds become unstable, and dissociate into lower boiling hydrocarbons, which, under the temperature control imposed in the vapor line, leave the distilling system as fast as produced; Al_2Cl_6 is again formed and is capable of combining further with other high boiling hydrocarbons remaining in the still, and free carbon is formed simultaneously. This view of the reaction here involved is thought to be confirmed by the operating conditions mentioned as necessary for obtaining the desired results.

While the operation, using crude oil as the starting material, can be carried on to produce larger or smaller quantities of gasoline, in practice it is conducted so as to convert the gas oil fraction into low boiling hydrocarbons and leave most of the high boiling hydrocarbons, that is, the paraffins and lubricating oils. Accordingly, the operation is interrupted after a portion of the crude has been converted into low boiling products, and the high boiling oil remaining in the still is pumped off while hot and on cooling is worked up into the usual paraffin and lubricating products. The aluminum chloride remains in the still enmeshed in a mass of coke.

As illustrative of the action of aluminum chloride on high boiling

petroleum oils, results are given below, obtained on typical crudes. For the sake of convenience, the distillate obtained by distilling the crude before the addition of aluminum chloride will be termed " primary distillate," the oil remaining in the still being termed " primary residual oil "; the distillate obtained by distilling the primary residual oil with aluminum chloride will be termed " secondary distillate " and the oil remaining in the still, " secondary residual oil."

The distillation tests were made on 100-c.c. samples contained in standard Engler flasks connected to a 22-inch Liebig condenser. All flash points noted are in open cup tester. Viscosities noted are on the Saybolt Universal Viscosimeter at 100° F. W.W. and S.W. are abbreviations for water white and standard white, respectively. Texas crude of 20.8 Bé. gravity was distilled until free from moisture and until the naturally occurring gasoline and kerosene had been distilled over.

	Yield	Per cent, Crude
Primary distillate	. . . .	7.14
Primary residual oil	. . . .	91 26
Loss..	. . . .	1.60
Total	. . . .	100 00

Tests on Primary Distillate

Gravity	. . . .	36
Bromine No.	. . . .	5.46
Distillation over		260° F.
10 %	. . . . . .	320
20 %	. . . .	344
30 %	. . . .	368
40 %	. . . .	386
50 %	. . . .	400
60 %	. . . .	442
70 %	. . . .	468
80 %	. . . .	490
90 %	. . . .	505
95 %	. . . .	520

The primary distillate yielded on fractional distillation the following products

	Per Cent Crude	Gravity Baumé	Color	Per Cent Sulphur	Bromine Number
Gasoline	0.303	58.0	W.W.	0 065	4 8
Gas naphtha ...	0.180	51.0	S.W.	0 103	3.1
W.W. kerosene .	1.260	41.6	W.W.	0.071	
S.W. kerosene	1.530	40.9	W.W.	0 133	
Gas oil	3.791	31.2	....	0 386	
Loss	0.076				
Total	7.140				

TESTS ON PRIMARY RESIDUAL OIL

Gravity... 19.8
Viscosity... 302

    Distillation over............................. 480° F.
    10 % 530
    20 %.. 566
    30 %.. 600
    40 %.. 656
    50 %.. 680

To the primary residual oil was added $7\frac{1}{2}$ per cent by weight of anhydrous aluminum chloride and the mixture brought to boiling. The following observations were made during the course of the run:

Time	Temp. of Still	Temp. of Vapor Line	Distillate, Per Cent Charge	Gravity Baumé	Distillation Test			
					Over Deg. F.	Per Cent Below 350° F.	Per Cent Below 450° F.	Dry Point
1 P.M.	454	268	Showed up					
1:30	479	290	2 86	55 9	110	68	80	490
1:45	488	300	2.86	55 2	110	69	84	490
2:15	495	302	2 86	54 4	110	66	80	490
2.45	504	290	2.86	54 1	110	66	81	490
3:15	508	290	2 86	53 5	110	65	80	490
4:15	518	340	2 86	53 7	110	65	80	490
4:45	523	340	2 86	53 7	110	65	83	490
6.00	525	310	2.86	53 5	105	60	82	490
7:00	530	344	2.86	53.3	100	58	81	490
8:30	530	340	2.86	53.5	100	58	81	490
10.30	542	310	2.86	53.2	100	60	83	490
1 A.M.	547	320	2 86	52.6	100	60	83	490
4.00	547	300	2.86	52 4	100	60	83	490
6:30	552	290	2 86	52.8	100	58	83	495
10.00	551	305	2.86	50 6	100	58	83	500
1 P.M.	557	302	8.57	49 7	100	55	85	510
	From Back Trap		1 39					

The operation was stopped at the end of twenty-four hours.

Yield	Per Cent Charge	Per Cent Crude
Secondary distillate	52.86	48 24
Secondary residual oil	31.14	28.42
Loss (gas and coke)	16.00	14.60
Total.............................	100.00	91.26

TESTS ON SECONDARY DISTILLATE

Gravity...51.1
Distillation over.................................... 100° F.

10 %	174
20 %	228
30 %	265
40 %	294
50 %	324
60 %	357
70 %	388
80 %	428
90 %	475
95 %	500

The secondary distillate on fractional distillation yielded the following products:

	Per Cent Charge	Per Cent Crude
Gasoline	38.18	17 45
Gas naphtha	26 62	12.85
W W. kerosene	2 65	1.28
S.W kerosene	9 53	4.59
Solar oil	21.80	10.52
Loss....	3.22	1.55
Total	100.00	48.24

The tests on the gasoline and the gas naphtha are as follows:

	Gasoline	Gas Naphtha
Color	W.W.	S.W.
Odor	Sweet	Sweet
Bromine No	4.2	3.2
Dr. test	O.K.	O.K.
Heat test..	4	3
Sulphur	0.056 %	0 054 %
Gravity	64 5 Bé.	50.2 Bé.

	Gasoline		Gas Naphtha	
	Deg. F.	Gravity, Bé.	Deg. F.	Gravity, Bé.
Distillation over	117	....	215	..
10 %	160	82 1	240	57.0
20	170	79 0	246	55 0
30	179	75 3	253	54.1
40	190	70.9	260	52 8
50	208	66 0	270	51 3
60	222	61 8	280	50 2
70	239	57 7	293	49.1
80	261	64 2	306	47.5
90	293	50 4	332	45 4
98 dry point	339	. ..	350	... .

The secondary residual oil obtained in the above process had the following tests, when freed of aluminum chloride:

Color....   . ... Red, green bloom
Flash   ... . 185° F.
Fire   250
Viscosity........ 105

This residual oil was reduced with steam in order to make lubricating oil.

Yield	Per Cent Charge	Per Cent Crude
Gas oil	10 00	2.84
Lubricating oil	90 00	25.58
Total	100 00	28 42

TESTS ON LUBRICATING OIL

Color .... Red, green bloom
Gravity................ ... . 21.9
Flash....................................... 290
Viscosity...................................... 122

SUMMARY OF YIELD OF PRODUCTS FROM TEXAS CRUDE BY
THE ALUMINUM CHLORIDE PROCESS

	Per Cent Crude
Primary gasoline	0.30
Secondary gasoline	17.45
Primary gas naphtha	0 18
Secondary gas naphtha	12.85
Primary kerosenes	2.79
Secondary kerosenes	5.87
Gas oil	17.15
Lubricating oil	25 58
Total	82.17
Loss account distilling primary distillate	1.60
Loss account distilling with aluminum chloride	14.60
Loss account redistillation of primary distillate	0 08
Loss account redistillation of secondary distillate	1 55
Total	100.00

The following table compares the yield of products from a Texas crude by the aluminum chloride process with the yield of products as obtained when the crude is distilled in the usual manner:

	Per Cent Crude Aluminum Chloride Process	Per Cent Crude Usual Process
Gasoline	17 75	zero
Gas naphtha	13 03	0 10
Kerosenes	8 66	4 30
Gas oil	17 15	52 00
Lubricating oils	25 58	25 50
Asphaltic residual oil		12 00
Total	82 17	93 90
Loss	17 83	6 10
Total	100 00	100 00

In ordinary practice no gasoline is obtained from this type of Texas crude; by the aluminum chloride process 17.75 per cent is obtained and this gasoline is as good as the natural gasoline made from any crude petroleum. The gas naphtha, which might very well be mixed with the gasoline, has been increased from 0.1 per cent to 13.03 per cent. It will be observed that these low boiling oils have been made at the expense of the gas oil fraction and the asphaltic residual oil, the

latter being broken down completely. Gas oil is the least valuable constituent of the crude. The asphaltic residual oil is used for fuel or is made into asphalt. The yield of lubricating oil by the aluminum chloride process is about the same as that in the usual process, but the quality of the former is said to be greatly improved by virtue of the saturating effect of the aluminum chloride and the elimination of asphaltic and resinous constituents from the oil.

A Caddo (Louisiana) crude of 41° Bé. was distilled to free it from moisture and natural gasoline.

YIELD	Per Cent Crude
Primary distillate	26.19
Primary residual oil	71.43
Loss	2.38
Total	100.00

TESTS ON PRIMARY DISTILLATE

Gravity	58 2
Distillation over	160° F.
10 %	215
20 %.	232
30 %	247
40 %	260
50 %	276
60 %.	296
70 %	315
80 %	343
90 %.	402
95 %	450
Dry point.	500

The primary distillate on fractional distillation yielded:

Yield	Per Cent Charge	Per Cent Crude
Gasoline	82.00	21.48
Kerosene	15 00	3.93
Loss	3.00	0.78
Total	100 00	26.19

Five per cent by weight of aluminum chloride was added to the primary residual oil and the mixture brought to boiling. Distillation was continued for forty-eight hours, the temperature of the vapor line at the point of exit into the final condenser being held around 350° F.

Yield	Per Cent Charge	Per Cent Crude
Secondary distillate	58.33	41.67
Secondary residual oil	26.20	18.71
Loss (gas and coke)	15 47	11.05
Total	100 00	71.43

TESTS ON SECONDARY DISTILLATE

Gravity (Baumé)...........	54.0
Distillation over.	102° F.
10 %....	212
20 %.....	260
30 %	293
40 %...	315
50 %	340
60 %	365
70 %	388
80 %	414
90 %	450
95 %	480
98 dry point....	500

The secondary distillate on fractional distillation yielded the following products:

Yield	Per Cent Charge	Per Cent Crude
Gasoline	50 00	20.84
Solvent oil	40 00	16.67
Gas oil	6 00	2.50
Loss................................	1 00	1.66
Total	100 00	41.67

Following are the tests on the gasoline and solvent oil:

	Gasoline	Solvent Oil
Color	W.W.	W.W.
Odor	Sweet	Sweet
Bromine No	2	3
Dr. test	O.K.	O.K.
Heat test	2	2
Gravity (Baumé)	58 0	48.1
Distillation over	120° F.	340° F.
10 %	198	354
20 %.	221	360
30 %.	240	364
40 %	258	369
50 %	272	374
60 %..	288	381
70 %	301	390
80 %.	322	400
90 %	348	416
95 dry point	362	430
98 dry point	...	440

TESTS ON SECONDARY RESIDUAL OIL

Color	Red, green bloom
Gravity	36 5
Flash	260° F.
Fire	300
Pour	90° F.

This residual oil was distilled until 30 per cent of the charge had been distilled over.

Yield	Per Cent Charge	Per Cent Crude
Gas oil	30 00	5.61
Paraffin residual oil	70 00	13.10
Total	100 00	18 71

TESTS ON PARAFFIN RESIDUAL OIL

Color	Amber
Pour	105° F.
Flash	375
Fire	420

SUMMARY OF YIELD OF PRODUCTS FROM CADDO (LOUISIANA) CRUDE OIL
BY THE ALUMINUM CHLORIDE PROCESS

	Per Cent Crude
Primary gasoline	21.48
Secondary gasoline	20.84
Secondary solvent oil	16 67
Primary kerosene.	3 93
Gas oil	8.11
Paraffin residual oil.	13 10
Total	84 13
Loss account aluminum chloride distillation .	12 71
Loss account working distillates into standard products....	3 16
Total	100 00

The following table compares the yield of products from Caddo crude by the aluminum chloride process and the yield of products as obtained in usual practice:

	Per Cent Crude Al₂Cl₆ Process	Per Cent Crude Usual Process
Gasoline	42 32	18 00
Solvent oil .	16 67	12 00
Kerosenes	3 93	35 00
Gas oil	8 11	21 00
Paraffin residual oil	13 10	11 00
Total	84 13	97 00
Loss	15.87	3 00
Total	100 00	100 00

This crude belongs to the same type as Pennsylvania crude — the type known as paraffin base crude. Their products are clean smelling and require but little acid in refining. But even this type of crude is considerably improved by the aluminum chloride process, while at the same time the yield of gasoline is greatly increased. The paraffin residual oil from Caddo crude is black and tarry on account of the presence of asphaltic constituents, but these are not usually present in large enough amounts to prevent the manufacture of good paraffin and paraffin lubricating oil. The distillation with aluminum chloride destroys the asphaltic constituents, giving an amber colored residual oil which may be easily worked into a product, commercially known as vaseline, or into paraffin and paraffin lubricating oils. At the same time the yield of gasoline from the crude is increased from 18 per cent to 42.32 per cent.

An Oklahoma crude of 34 gravity was distilled to free it from moisture and natural gasoline.

	Yield	Per Cent Crude
Primary distillate	....	20.83
Primary residual oil.	....	78 31
Loss.......	....	0 86
Total	....	100.00

TESTS ON PRIMARY DISTILLATE

Gravity (Baumé)	....	54.1
Color	....	W.W.
Distillation over	....	152° F.
10 % ..	....	210
20 %	....	226
30 % .	.. ..	242
40 %	... .	252
50 %	.. . .	271
60 %	.. . .	290
70 %	. ...	313
80 %	.. ..	345
90 %	.. . .	408
95 % dry print		455

This primary distillate on fractional distillation yielded the following:

Yield	Per Cent Charge	Per Cent Crude
Gasoline	70 00	14.58
Kerosene	20 00	4 17
Gas oil	7.50	1 56
Loss	2 50	0 52
Total	100 00	20 83

TESTS ON PRIMARY RESIDUAL OIL

Color	.... Black	Distillation over	330° F.
Gravity (Baumé).... ..	29 8	10 %	436
Flash	 170	20 %	484
Fire	205	30 %	543
Pour	20	40 % .	590
		Below 600° F.........	43 %

To the primary residual oil was added 5 per cent by weight of aluminum chloride. Distillation was then continued for a period of forty-eight hours, the temperature of the vapor line at the point of exit into the final condenser being held around 350° F.

	Per Cent Charge	Per Cent Crude
Secondary distillate	64.61	50.60
Secondary residual oil	17.97	14 07
Loss.........	17 42	13.64
Total	100.00	78 31

TESTS ON SECONDARY DISTILLATE

Gravity (Baumé)....	48 3
Distillation over.	140° F.
10 %	225
20 %.	270
30 %	294
40 %	326
50 %	. 358
60 %	. 382
70 %	413
80 %.	454
90 %.	503
95 %	517
98 % dry point	570

On fractional distillation this secondary distillate yielded the following:

	Per Cent Charge	Per Cent Crude
Gasoline	40 00	20 24
Kerosene	50.00	25 30
Gas oil	7.50	3.80
Loss...	2 50	1 26
Total	100.00	50.60

TESTS ON GASOLINE

Color	W.W.	Distillation over .. .	130° F.	Gravity
Odor.	Sweet	10 %	160	83.8
Bromine No	1.5	20 %	186	76 2
Dr. test.	O.K.	. 30 %	200	70.1
Heat test .	2	40 %.	213	66.6
Sulphur	.027	50 %	222	62.8
Gravity (Baumé)....	64.5	60 %.	238	60.4
		70 %	252	58.5
		80 %	270	56.1
		90 %	299	53.3
		Residue	8.3 %	48.2

Color.. Red, green bloom.

Gravity (Baumé). 28.2

Pour.. .... 90° F.

Flash... 230° F.

This secondary residual oil was distilled to produce wax stock and cylinder oil.

Yield	Per Cent Charge	Per Cent Crude
Wax stock	60 00	8.44
Cylinder oil	40.00	5.63
Total.......	100.00	14.07

Summary of Yield of Products From Oklahoma Crude by the Aluminum Chloride Process

	Per Cent Crude
Primary gasoline	14 58
Secondary gasoline	20 24
Primary kerosene	4.17
Secondary kerosene	25 30
Gas oil	5 36
Residual oil	14 07
Total	83 72
Loss account aluminum chloride distillation	13 64
Loss account working distillate into standard products	2.64
Total	100.00

The following table compares the yield of products from Oklahoma crude by the aluminum chloride process and the yield of products as obtained in usual practice:

	Per Cent Crude Aluminum Chloride Process	Per Cent Crude Usual Process
Gasoline	34 82	12.50
Kerosenes	29.47	41.00
Gas oil	5.36	35.00
Residual oil................	14.07	9.00
	83.72	97.50
Loss....................	16.28	2.50
Total....................	100.00	100.00

The residual oil from this crude by the usual process is a black, tarry mass, containing a large amount of asphaltic constituents and also paraffin. The amount of asphaltic constituents is so great, as a rule, that it is difficult to make paraffin and paraffin lubricating oils of the same grade as that obtained from Pennsylvania or Caddo residuums. By the aluminum chloride process this residual oil is cleaned of its asphaltic constituents, and paraffin wax and paraffin lubricating oils of excellent quality are made therefrom. At the same time, the yield of gasoline from the crude is greatly increased, at the expense of the less valuable fractions of the crude.

Although the crude petroleums from the various oil producing districts in this country differ greatly in quality and in chemical composition, yet they are generally divided into three types: Asphaltic-base crude, paraffin-base crude, and paraffin-asphaltic-base crude. The oils mentioned are representative of each of these types: Texas, asphaltic-base crude, Caddo, paraffin-base crude, and Oklahoma, paraffin-asphaltic-base crudes.

All the good results of this process would be of no commercial value if the aluminum chloride could not be reclaimed. This chemical when made on the ton scale is not so expensive as it is when made on the pound scale, but nevertheless its cost is high, and from a dollars and cents point of view, it is necessary to recover it. After a time, forty-eight hours or longer, aluminum chloride used in distilling oils, even the driest of oils, loses its catalytic activity and becomes converted into a coky mass. Analysis of the coky mass shows chlorine and aluminum present in the right proportions to form aluminum chloride, but the latter is, so to speak, masked. It does not display its ordinary reaction with petroleum hydrocarbons. The granular coky residue, after it comes from the oil converting process, carries varying amounts of oils with it. If allowed to cool down in the presence of the body of oil, 'it may carry 40 to 50 per cent of its weight of oil. If the oil body has been separated while hot from the coky residue, the amount of oil will be reduced to 4 or 5 per cent.

After removing the oil, or the bulk of it, from the coky residue, the aluminum chloride can be extracted from the latter with water or steam to obtain a concentrated solution of hydrated aluminum chloride. Aluminum chloride in the hydrated state does not have the catalytic property of the anhydrous material; but the hydrated salt can be used as the raw material for making the anhydrous salt. To do this, advantage is taken of the property of hydrated aluminum chloride breaking up when moderately heated to form aluminum oxide and hydrochloric acid gas. The alumina, when mixed with carbon and

treated with hydrochloric acid vapors at a high temperature, reacts to form the anhydrous chloride, hydrogen and oxides of carbon. In utilizing this property, one portion of the hydrated chloride is heated to produce hydrochloric acid vapors and alumina, and these vapors on drying enter a further charge of alumina and carbon heated to redness. The hydrochloric acid vapors given off at a moderate temperature are thus utilized in further operations at high temperatures.

In another method of recovery, and the preferred one, the coky residue is heated to red heat in an atmosphere of chlorine which disengages the aluminum chloride from the carbon. Aluminum chloride volatilizes normally at a temperature around 365° F. but the coky residue may be heated to redness without much evolution of these vapors. If the heating is done in an atmosphere of chlorine, the aluminum chloride is unlocked, so to speak, and vaporizes away from the carbon, and is condensed in suitable receivers.

McAfee [1] states that he obtains a substantially complete catalytic conversion of higher boiling petroleum oils into lower boiling oils and in particular converts high boiling oils, distillates and residua into gasoline " solvents " and kerosene, or into gasoline alone by heating the high-boiling oil in a slow and regular manner in the presence of aluminum, while a current of chlorine or chlorine in combination such as hydrochloric acid gas is introduced into the oil, the low-boiling products of the reaction, and the hydrochloric acid produced being removed continually during the progress of the reaction and the volume of the oil being kept constant by the addition of fresh oil from time to time.

It has been found that by taking any high boiling petroleum oil, whether a crude oil, a distillate, or a residuum, suspending in it finely powdered aluminum, heating to a relatively moderate temperature, and introducing chlorine, the complex hydrocarbon molecules can be broken down into simpler molecules of the order of those found in gasoline, solvent oils and kerosene; by this method, a conversion of high-boiling oils into low-boiling oils takes place without a wasteful production of low-grade by-products. By regulating the conditions, the higher-boiling oils can be converted into gasoline alone. The amount of metal necessary is quite small. Most of the chlorine introduced reappears as hydrochloric acid gas, which may be condensed and utilized. In this reaction the low-boiling oils produced appear to be of saturated nature and are therefore of high grade. They do not contain any chlorine. The best metal that has been found for the purpose is aluminum. Hydrochloric acid may be used instead of

[1] U. S. Patent 1,235,523, July 31, 1917.

chlorine; in fact, in certain cases its use seems to be more advantageous than chlorine. The use of both is often convenient, since as the chlorine led into one apparatus reappears as hydrochloric acid, this acid may be used in another apparatus operating in parallel. Generally somewhat higher temperatures are advantageous, it is stated, in working with hydrochloric acid.

Aluminum in the form of " aluminum bronze " powder is particularly suitable as it is fine, light and readily distributed through the oil and presents enough surface to enable stirring apparatus to keep it in a state of uniform suspension. Either aluminum containing a little zinc or pure aluminum may be used. Where pure aluminum is available, it is sometimes a convenient expedient to grind up filings of it with coke, as this gives a large surface to the aluminum. Aluminum amalgam is particularly active. Instead of metallic aluminum, dry but reactive forms of alumina may be used, such as the dry, but unignited hydrate. This is said to be particularly true where hydrochloric acid is used.

The operation is carried out continuously in order to keep the oil in the apparatus of constant composition and at a constant temperature. The body of hot or boiling liquid oil in a still contains the powdered aluminum which is kept in suspension by vigorous agitation. Chlorine is led into contact with the oil. From the hot oil under treatment, the vapors of the low boiling products are withdrawn as fast as produced and are continuously drawn off and condensed. This is to remove the low boiling bodies from the influence of the catalytic operation.

The high boiling oils contain many constituents and while these do not all react with the same ease, or the same speed, yet under the described conditions any difficultly reacting body is simply retained in the still until it is converted and removed.

The time factor is important. The body of oil should be relatively large in comparison with the amount fed in and the amount distilled off in the unit of time. This insures ample time for the treatment of refractory constituents of the oil In continuous distillation where the volume of oil in the still is maintained constant by the influx of hot, fresh oil, refractory portions of the oil may remain in the still under the influence of the catalyst for two or three days. The temperature to be maintained in the oil should be as uniform as possible, but the particular degree will depend somewhat upon the oil being treated With high-boiling oil, such as gas oil, lubricating oil, still-bottoms, etc, normally boiling at or above 600° F, the average temperature during operation is very advantageously around 500° F. With such oils 600° F. may be stated as an extreme temperature, and around 500° F. as the best temperature. At 500° F. there is little or no danger of the ordinary type of cracking distillation taking place while with most of these oils, under the conditions of the above operation, there will be lively ebullition and distillation. The gasoline, solvent oils and kerosene formed vaporize freely from

the heavy oil around 500° F. The catalytic action on the extremely high boiling oils at temperatures below 500° F. is slow. At temperatures above 600° F. there is liable to be too much evolution of vapor, while there is also danger of cracking distillation taking place simultaneously with the catalytic action. Prior to allowing the vapors produced to go to the condensers, there should be an opportunity for condensation and return of heavy boiling vapors, by means of reflux condensers. (See *A* and *B*, Fig. 162.) As a rule the temperature of the vapors at the point of exit from the reflux condensers (see *C*, Fig. 162) should not exceed 350° F. The chlorine or hydrochloric acid gas is fed into the still by a duct, as for example *D*,
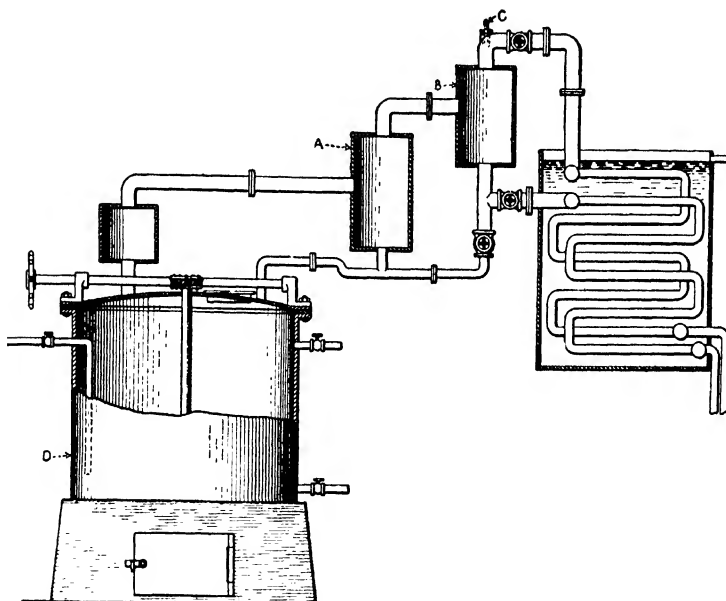
Fig. 162. — Diagram of McAfee's apparatus for treating oils with metallic aluminum and chlorine or hydrochloric acid.

Fig. 162. The process is stated to be applicable to any petroleum oil distillate or residuum. It enables a good utilization of gas oil, fuel oil and spindle oil. Kerosene may be converted by this method into gasoline. The proportion of the aluminum necessary is not large and it appears to maintain its activity for a considerable length of time, that is from two to three days of continuous distillation. For most oils less than one per cent of powdered aluminum (reckoned upon the amount of oil temporary in the still) is an efficient amount. Toward the end of the activity of a charge, the aluminous material is contained in a coky, granular mass.

It is stated that gas oils and similar oils have been converted into gasoline with about an eighty-five per cent conversion. About ten per cent of the oil is converted into gas, and the residue forms granules of coky carbon. As to the mechanism of the reactions occurring in the stills, it may be that some of the

catalytic action is due to the direct production of aluminum chloride in the body of oil, or it may be that the action of the aluminum on the oil in this operation is direct. It may be said, however, that the aluminum appears to exercise more catalytic activity in this process than would result from the corresponding amount of aluminum chloride.

McAfee[1] notes that among commercial petroleum products those which contain any considerable amount of unsaturated hydrocarbons are of lower grade of value than those which are free, or relatively free, of unsaturated hydrocarbons. A lubricating oil containing any substantial amount of unsaturated oils is apt to be dark colored, or to become so on standing; it is also prone to absorb oxygen from the air with discoloration, gumming, etc. In use on a hot bearing these difficulties are of course accentuated. Similar difficulties obtain in the case of gasoline, kerosene, paraffin wax and other petroleum oils and products. On heating a high-boiling petroleum oil, such as lubricating oil, a gas oil or solar oil, kerosene, etc, with aluminum chloride the latter, under proper conditions, will convert the whole of such high boiling oil into lower boiling oils of the nature of gasoline, with from about ten to fifteen per cent loss as gas and coke. All the distillation products of such an action will be found to be of saturated nature regardless of the composition in this respect, of the original high-boiling oil treated.

It is stated, moreover, that by treating a high boiling highly unsaturated oil with aluminum chloride at a relatively low temperature, a saturation of the unsaturated constituents is produced without the production of lower boiling oils. The temperatures necessary for this action are around 150° F. This warming-up treatment with anhydrous aluminum chloride may be applied to the improvement of any petroleum product. Gasoline and kerosene so treated have better burning qualities and better color; and the color does not again darken by exposure to air and light.

In saturating petroleum materials by this method, the oil is mixed with a small amount, about 2 to 5 per cent, of anhydrous aluminum chloride and vigorously agitated at a moderate temperature, in the neighborhood of 150° F. until the saturating action has progressed to the desired extent. The extent of the saturating action is measured by its iodine absorption value. To obtain the same amount of saturation requires a longer time with a heavy oil of the character of lubricating oil than with a lighter oil like kerosene or gasoline. The oil should be dry before admixture with the aluminum chloride and it is desirable to free it of sulphur compounds. Both moisture and sulphur compounds cause a waste of aluminum chloride, and in their presence undesired side reactions may occur. Vigorous agitation is necessary, because the aluminum chloride tends to settle out. The activity of the aluminum chloride gradually diminishes during the course of the

[1] United States Patent 1,277,329, Aug. 27, 1918; see also United States Patents 1,277,328 and 1,277,092, Aug. 27, 1918.

reaction, however, after having lost some degree of its activity in this way, it is still sufficiently active to be used in the production of gasoline from gas oil, kerosene, etc., at higher temperatures. The catalytic saturating action is more rapid at first when the proportion of unsaturated hydrocarbons is high than it is after a time when the percentage of the unsaturated bodies becomes very small. For improving a lubricating oil in this manner a treatment of from two to four hours is all that is necessary. For attaining the same object in the case of kerosene and gasoline the time required is less. The oil treated may be that coming from any crude oil whether paraffin base, asphalt base or naphthenic in character.

After the completion of the aluminum chloride treatment of oils containing any considerable amount of unsaturated hydrocarbons, the resulting oil should be further purified. Most of the aluminum chloride, but not all, will settle out as a sludge upon cooling the mixture and that which remains in suspension and in solution must be removed. The oil at this stage is not decolorized, but on the other hand is usually blackish or reddish in color from the presence of dissolved and suspended aluminum chloride compounds. The oil is then treated with sulphuric acid. One or two per cent by volume of the strong acid will suffice. After the acid treatment, ample time should be allowed for setting and depositing the compounds formed by the acid. This is followed by washing with caustic and water in the usual manner.[1]

Gray [2] also uses aluminum chloride. One form of his apparatus is shown in Fig. 163. A is the still. B is a shaft rotated by pulley C and gear D. The shaft B carries stirring blades, EE', the lower blades E' carrying depending chains F. G are splash plates attached to the shell of the still. H is a manhole and I a discharge opening at the bottom. J is the vapor exhaust pipe and K is an inlet pipe for oil and chemicals. The pipe J leads to a chamber N from which a vapor pipe O leads to the condenser. The chamber N represents diagrammatically one or more cooling chambers.

For example, 100 parts of petroleum distillate freed from naphtha products (such as gas oil made from a paraffin or semiparaffin or semiasphalt crude oil) are taken and to it is added five parts of anhydrous aluminum chloride. The mixture is then heated to a temperature

[1] For the manufacture of aluminum chloride and recovery of aluminum chloride residues see McAfee, U. S. Patent 1,099,096, June 2, 1914; U. S. Patent 1,202,081, Oct. 24, 1916; U. S. Patent 1,206,874, Dec. 5, 1916; U. S. Patent 1,217,471, Feb. 27, 1917. See also McAfee; J. S. C. I. 1916, 1430 and 298; British Patents 22,243 and 22,244, Nov. 9, 1914, 22,924, Nov. 23, 1914.

[2] J. S. C. I. 1914, 1044; U. S. Patents 1,193,540, and 1,193,541, Aug. 8, 1916; British Patents 17,838 and 17,839, Aug. 5, 1913.

above the end boiling point of naphtha. So long as the hydrocarbons in the still are not heated to produce a vapor temperature above the end boiling point of naphtha — about 400° F.— the vapors driven off will contain little or no illuminating oil, or hydrocarbons of higher boiling point than naphtha; but, when the temperature is increased above that point, illuminating oil will be driven off, and this will be condensed in the cooling chamber, or chambers, indicated by N, so that only naphtha or gasoline will pass to the condensing chamber. If it is desired to convert all the oil into naphtha, the illuminating oil collected in the chamber N is returned to the still by the pipe M, where it is again acted on by the aluminum chloride and heat. The higher the tem-

Fig. 163. — Gray's apparatus for treating oils with aluminum chloride.

perature employed above the end boiling point of naphtha, the larger will be the percentage yield of illuminating oil and the smaller will be the percentage yield of naphtha.

If a temperature much higher than the end boiling point of illuminating oil be employed in the still, the catalytic agent will be driven off, resulting not only in the loss of that agent, but also in clogging the pipes. The still is provided with stirring apparatus such as the blades E, E' and the chains F, to keep the aluminum chloride in suspension and in intimate contact with the oil and to prevent overheating it. Fresh charges of oil are added from time to time through the inlet K to avoid distilling the contents to dryness and to obtain the advantage of the repeated use of the catalyzer, the efficiency of which appears to persist for a considerable time. If the charge were distilled to dryness, the catalytic agent would be lost, coke would be formed and cleaning the still after each charge would be required.

If desirable, additional aluminum chloride may be added from time to time as required. The use of a larger percentage than that named in the above example — 10 parts to 100 parts of oil, for example — causes the desired reactions to take place much more rapidly. The process above described may also be practiced with illuminating oil or lubricating oil as starting materials. It may also be practiced with crude oils as the starting material, but it is less advantageous to use crude oil because of its contained impurities.

There is a demand, according to **McAfee,**[1] for gasoline distilling
within a narrower temperature range than that of ordinary gasoline,
which as it now occurs on the market may begin to distill at 120° F.
(49° C.) and have an end point of 350° F. (176° C.). To convert
material of this nature into a more uniform product possessing a lower
boiling range it is distilled in aluminum chloride, the still being pro-
vided with a reflux condenser: the latter is maintained at a definite
temperature, namely that corresponding to the end point of the gasoline
which is desired, for example say 200° F. (93.5° C.). By returning to the
still all products boiling higher than the temperature of the reflux
condenser the naphtha which distills over, and which is formed by the
breaking down of the heavier portions of the gasoline, possesses a com-
paratively narrow boiling range and one which is considerably lower
than that of the original material.

This treatment may be applied to the " light distillate " from pres-
sure stills or to the naphtha obtained by re-running the light distillate.

McAfee emphasizes the fact that if it is desired merely to convert unsaturated
naphtha into a more saturated product, that this may be accomplished by simply
warming naphtha with aluminum chloride at a temperature of about 120° F. (49° C.)
to 150° F. (65.5° C.), stirring vigorously and discontinuing the operation when the
desired degree of saturation is obtained (as indicated by the iodine test).

Recently [2] McAfee combines the application of the aluminum chlo-
ride process with the action of an ordinary pressure still in such a way
that the yield of light naphtha from the latter is said to be materially
increased. For example a charge of gas oil and aluminum chloride
in a suitable still is brought to the boiling point. Another charge of
gas oil is contained in an ordinary cracking still which is operating under
pressure and the vapors from this cracking operation will lead directly
into the boiling mass of oil and aluminum chloride. The still contain-
ing the aluminum chloride is provided with a reflux condenser main-
tained at a temperature which will insure that vapors passing through
it possess a sufficiently low boiling range, for example 350° F. (176° C.).
McAfee states that by this combination of pressure still operating
in series with body of oil containing aluminum chloride that a much
larger amount of gasoline vapor is delivered to the final condenser in
a given time. Part of this gasoline comes from the transforming
action of the chloride upon the gas oil in the aluminum chloride still;
part comes from the vapors fed in from the pressure cracking still;
but according to McAfee, it is all uniform, clean, good quality saturated
gasoline.

[1] U. S. Patent 1,326,072, Dec. 23, 1919.
[2] U. S. Patent 1,326,073, Dec. 23, 1919.

McCarty [1] treats petroleum oils having boiling points higher than gasoline with an aqueous solution of aluminum sulphate or alum and then agitates the oil with steam under 150 pounds pressure. Five per cent of water containing five per cent of aluminum sulphate or alum is added to the oil. The receptacle is then hermetically sealed and superheated steam under a pressure of about 150 pounds per square inch is introduced for a period of from fifteen to thirty minutes. The steam is shut off and the water contained in the oil is allowed to settle and is drawn off. The alum acts as a refining agent, to drag down tarry matter and other impurities in the oil, which are removed from the oil when the water is withdrawn. After withdrawal of the water, steam is again introduced into the oil under a pressure of 150 pounds per square inch until the temperature is raised to 250° to 300° C.° (257°–572° F.). The treated oil then passes through a superheating coil maintained at a temperature of 400° C. (752° F.). It is intimately mixed with hydrogen in the proportions of one part by weight of hydrogen to 500 parts by weight of the vaporized oil. The proportion of hydrogen used should be in excess of the amount necessary to saturate the unsaturated molecules. The mixture is then passed into and through a cracking tube which is maintained at a constant temperature of 600° C., and in this cracking tube the mixture is subjected to the action of nickel. The pressure in the cracking tube or retort is maintained at about fifty pounds per square inch. Under these conditions the petroleum material under treatment is decomposed with the production of gasoline, benzol and toluol and, it is claimed, a minimum production of gas, carbon and tarry matters.

The products of decomposition are passed from the cracking tube into a condenser where the condensable hydrocarbons are separated, and the gaseous portion of the decomposition products is collected in a gas holder. The cracking tube contains an axially located rod to which a number of scrapers are attached, as shown in Fig. 165, in vertical section and Fig. 164 in horizontal section. Both the rod and attached scrapers have nickel surfaces or are made of nickel entirely. The rod has both a longitudinal and rotatory motion. The catalytic body, therefore, acts also as a scraper and removes carbon from the walls of the tube.
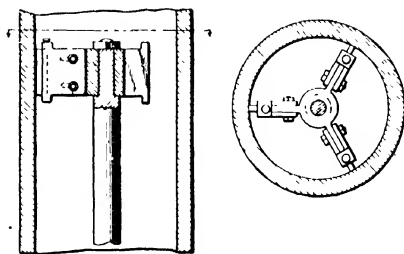
Figs. 164 and 165. — Cracking tube with scrapers, devised by McCarty.

[1] J. S. C. I. 1918, 617A; U. S. Patents 1,274,912 and 1,274,913, Aug. 6, 1918.

The Continental Caoutchouc and Gutta Percha Company [1] break up
heavy oils, without the use of pressure, by means of aluminum organo-
metallic compounds. No free aluminum chloride is used, that is, the
organo-metallic oily compound is prepared before using it in the crack-
ing operation.[2]

It is stated that the oily reaction products described by Gustavson
and obtained from halogen compounds of aluminum and hydrocarbons
or halogen alkyls and which are called "hydrocarbon halogen alumi-
num" are capable alone, without free aluminum halogenide, without any
"hydrocarbon" and without any halogen alkyl, of splitting up mineral
oil (paraffin) and its fractions after the manner of a ferment and in a
continuous catalytic process, while they themselves suffer scarcely any
change during the reaction. By means of small quantities of these
oils, mineral oils can, it is stated, be converted into benzine-like sub-
stances both at ordinary as well as increased pressure and even under

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[1] J. S. C. I. 1915, 826; British Patent 7112, Mar. 20, 1914; Int Conv. Mar. 22.
1913.

[2] The following review of previous work in this direction is given as leading up
to the use of the oily organo-metallic compounds for oil cracking

"Friedel and Crafts showed that aluminum chloride is capable of splitting
up paraffin hydrocarbons and they obtained, in the presence of aluminum chlo-
ride, metallic oxides and air, a mixture of gases, oils and products containing
paraffins (Engler and v. Hofer, 'Das Erdol,' 1 (1912), p 563). According to
Lothar Meyer and Köhnlein, paraffins can also be obtained from the correspond-
ing alkyl iodides by means of aluminum chloride (Ber. 1883 (16), 561) The re-
action however was in particular investigated by Gustavson. This investigator
allowed hydrogen bromide and aluminum bromide to act upon alkyl halogenides,
ethylene and paraffin compounds, and he found that under certain experimental
conditions the aluminum bromide becomes converted into a thick oil which is
not decomposed by water into the raw materials and is known as the so-called
hydrocarbon aluminum bromide (Meyer-Jocobson, Lehrb. d. organ Chem 1,
[i] (1907), 836). He also found that gaseous and partially unsaturated products
were produced. Similar results were obtained by Friedel and Gorgeu, from whose
work it appears that in Gustavson's reaction gaseous constituents and a brown,
viscous compound were produced from hexane Gustavson then investigated the
Friedel and Crafts method of alkylation, with the view of determining the nature
of the intermediate products (Centralbl 1903, I, 1333 and 1379). He found as a
result that the complex intermediate products were capable of exerting an inter-
esting 'ferment action' with aromatic compounds. Accordingly there is formed
from aluminum chloride, ethyl chloride and benzene for example, a product for the
composition for which he assumes the following formula

$$[Al_2Cl_6C_8H_{16}] \quad [6C_6H_6]$$
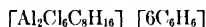
and in which only the left-hand component is stable, while the one on the right
hand can be split off and alkylated with the separation of hydrochloric acid, so
that the left-hand component is capable of reacting again in analogy with the
amorphous ferments."

reduced pressure and at relatively low temperatures, the boiling temperature being in no case exceeded.

The action of the aluminum oils which are obtainable according to Gustavson's methods from saturated or unsaturated hydrocarbons, or alkyl chlorides, takes place, it is noted, without difficulty. The oil may be supplied to the process in a finely divided solid form by allowing it to be absorbed by porous or similar compositions with large surface attraction.

Example

1. In a still are heated 1000 parts of mineral oil (such as high boiling petroleum for example), with 50 parts of "*hydrocarbon aluminum chloride*" and the mixture raised to boiling so that the light oils formed distill off continuously at about 110° C. (230° F.). The higher boiling portion flows back and is gradually completely decomposed. From time to time small quantities of fresh catalyst are added in order to revivify the process. The benzine obtained contains traces of hydrochloric acid, which can be removed by means of lime In proportion as the light oil passes over the heavy oil is allowed to flow in The process can be carried out under reduced pressure at about 130 millimeters

A compound of aluminum chloride and hydrocarbon is also employed by **R. Koetschau** [1] as catalyst in the decomposition of relatively heavy petroleum hydrocarbons into hydrocarbons of lower boiling point. The catalyst may be formed in the oil by reaction between aluminum and hydrochloric acid gas, with or without the use of mercuric or ferric chloride. The catalyst may be mixed directly with the oil to be treated or may be absorbed by kieselguhr and used in the form of a layer over or through which the vapors of the oil undergoing treatment may be passed. Ultraviolet light is suggested as a means for increasing the velocity of the action.

The **Continental Caoutchouc and Gutta Percha Company** [2] also heats a mineral oil fraction of high boiling point with a catalyst such as aluminum chloride, or with aluminum chloride and mercuric, ferric, or vanadium chloride, or with aluminum in a stream of dry hydrochloric acid gas; or the oil is atomized and exposed to ultraviolet rays or the silent electric discharge in the presence of the catalyst.[3]

[1] Chem. Abs. 1920, 466; U. S. Patent 1,325,299, Dec. 16, 1919.

[2] Chem. Abs. 1915, 19; French Patent 469,948, Mar. 21, 1914. See also Swedish Patent 41,840, Jan. 10, 1917.

[3] H. Hibbard (Chem. and Met. Eng. 1919, 339) states that the cracking of petroleum has been developed to a remarkable extent, but it would seem that there is still room for processes involving the use of other contact materials which would enable this operation to be carried out at both a lower temperature and pressure. Possibly additional research would show the advantage of metallic chlorides other than aluminium. The reactions of hydrocarbons with sulphur chlorides,

It appears that the action of " nascent " hydrogen, generated by the action of suitable metals on hydrochloric acid may play a part in the decomposition of oils by the " aluminum chloride process." It is well known also that the action of many anhydrous chlorides on unsaturated hydrocarbons gives rise to the production of hydrochloric acid. **Meigs** [1] makes observations to this effect in the action of sulphur chloride on unsaturated hydrocarbons. It may be that some of the organo-aluminum compounds formed from aluminum chloride and unsaturated hydrocarbons yield, in the aluminum chloride process, metallic aluminum momentarily, which reacts with hydrochloric acid to regenerate aluminum chloride and hydrogen.[2] If this theory has any truth, it would mean that the chlorine acts merely as a carrier of hydrogen and that the aluminum is the " activator " of the hydrogen, that is, causes the liberation of energized hydrogen from the hydrochloric acid. That hydrogen is transferred from some hydrocarbons to others, in the aluminum chloride process for making gasoline, is suggested by the production of coke or bodies with high carbon content. It may also be noted in this connection that the simultaneous use of chlorine and hydrogen is a recent proposal. The actual proven presence of metallic aluminum and hydrochloric acid would, of course, necessitate the accompaniment of more or less so called " nascent " hydrogen.

E. B. Cobb [3] observes that when gas oil is heated with say not more than 10 per cent by weight of aluminum chloride that the latter dissolves in a portion of the gas oil and that the solution thus obtained forms a distinct layer underneath the main body of oil treated. It is therefore necessary, in order to obtain suitable reaction between the two liquid layers, to employ efficient agitation.

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it is said, would also repay investigation, and the interesting experiments recently carried out with nitrosyl chloride (J Amer. Chem Soc. 1919, (41), 368) are stated to possess much interest both for the scientist and for the technical chemist.

[1] J. Ind. Eng. Chem. 1917, 655

[2] When cracking solar oil in the presence of ferric chloride or aluminum chloride **A. P. Lidoff** (J. S. C. I. 1919, 402 A; Petroleum, 1917, 12, 413–427; Chem. Zentr. 1919, 90, II, 290) considers it advantageous to form the anhydrous catalyst during the process. For this purpose the oil is mixed with iron or aluminum and a current of hydrogen chloride gas passed through the mixture. The resulting " nascent " hydrogen is supposed to promote the formation of saturated compounds. The process takes from 2 to 3 hours at 250° to 280° C. (482° to 536° F.). In this way solar oil treated with iron as catalyst yielded 65 per cent of distillate of specific gravity 0.865, while with aluminum as catalyst the yield was 70 per cent. The decomposition products are reported by Lidoff to be saturated compounds of pleasant odor, and to not alter in the air. The highest yield of aromatic compounds is obtained by cracking at 600° C. (1112° F.) under a pressure of 18 atmospheres.

[3] U. S. Patent 1,322,878, Nov. 25, 1919.

Distillation is conducted so that the temperature of the charge undergoes a continual increase. For example, a still is charged with 400 barrels of gas oil and 7 to 10% of aluminum chloride added. The temperature is gradually raised until distillate commences to flow from the condenser outlet; and the fires are regulated to give a good flow, for example 15 to 20 barrels an hour or thereabouts. Cobb observes that if distillation is stopped at a suitable stage it becomes possible to recover substantially all the aluminum from the oil residue by washing the latter with hot water. If distillation proceeds very much beyond this point, it is then advisable to distill to coke and roast the residue to convert the aluminum into its oxide.

A. E. Houlehan [1] makes toluol by treating xylenes (commercial xylol) with aluminum chloride, allowing toluol to escape from the reaction zone as fast as formed.

In another process of Houlehan [2] solvent naphtha is treated with aluminum chloride and the lower boiling hydrocarbons formed are distilled off under vacuum as fast as they are generated.

Danckwardt [3] proposes to generate aluminum chloride and hydrogen in contact with a mass of oil, in order to produce saturated low boiling hydrocarbons from high boiling oils. This is accomplished in part by the action of aluminum, reduced from its oxide, on hydrochloric acid, in the form of gas or vapor. Previously formed aluminum chloride is used, in addition to that generated in contact with the oil. Metals other than aluminum are also used for generating " nascent " hydrogen in the presence of hydrochloric acid gas and liquid oil, for example, zinc, iron, lead, nickel, antimony.

According to a method proposed by **A. E. Miller** [4] oils which have been treated with aluminum chloride and which contain suspended or dissolved aluminum chloride are air-blown until the latter is converted into such a form that it readily settles out. According to Miller these colloidal suspensions may be destroyed by treatment with a very small amount of sulphuric acid. Flocculation or coagulation may also be obtained by filtration through fuller's earth, or treatment with sulphuric acid may be followed by filtration through fuller's earth. Miller also notes that small amounts of alkalies induce flocculation, for example ammonia, sodium carbonate, or bicarbonate. However, the simplest method is stated to be treatment of the colloidal suspensions with moist air. This is accomplished by blowing with naturally humid

[1] U. S. Patent 1,334,033, Mar. 16, 1920.
[2] U. S Patent 1,337,317, Apr. 20, 1920.
[3] U S Patent 1,317,077, Sept. 23, 1919.
[4] Chem. Abs. 1919, 2610; U. S. Patent 1,311,987, Aug. 5, 1919.

atmospheric air. A more rapid method is blowing atmospheric air through hot water and then introducing the humidified air into the oil. Miller believes that a still quicker method is to use steam with air, introducing it through a small orifice and agitating the oil with the stream for a few seconds.

Charitschkov[1] has studied the action of aluminum on petroleum hydrocarbons.

Strips of pure aluminium were almost completely immersed in distillates from petroleum, solar oil, and benzene, and in petroleum spent acids for four months at the ordinary temperatures. With the exception of that exposed to the action of benzene, which had increased in weight 0 08 per cent and become slightly spotted, none of the strips, it is stated, were acted upon. Charitschov suggests the lower molecular weight of benzene as the possible explanation of its greater reactivity. At temperatures of 75° to 80° C (167°–176° F.), and 100° to 120° C. (212°–248° F.), the strips in the petroleum distillate and crude petroleum were intact after 48 hours, but after heating at 175° to 180° C. (347°–356° F.) for 38 hours under a reflux condenser, the aluminium in each case had increased in weight in the petroleum distillate by 0.016 per cent and in the petroleum by 0 017 per cent. From these results Charitschkov considers pure aluminium superior to copper and equal to iron, in its power of resisting the action of petroleums It is said to be specially suitable for vessels, such as cooling tanks, etc., in which the temperature of the petroleum does not exceed 120° C. (248° F.). Obviously the oil must be freed from any alkali, which, if present, would increase the solvent power.

Tests conducted by **Cross**[2] with many catalytic bodies including aluminum powder, nickel, copper, mercury, zinc dust, iron dust, and platinized pumice did not, it is observed, afford increased yields of light hydrocarbons from heavier oils.

B. T. Brooks[3] converts solvent naphtha containing a large percentage of xylenes into toluene and benzene by refluxing the crude materials with aluminum chloride, regulating the temperature of the reflux condenser in such a way that toluene and benzene vapors are allowed to escape as fast as formed while heavier hydrocarbons are returned for further treatment. The action of aluminium chloride on the aromatic hydrocarbons appears to cease as soon as equilibrium conditions are attained, and by destroying this equilibrium by removing the products of reaction, namely toluene and benzene, the yields of the latter bodies are increased.

Macnicol[4] uses an apparatus consisting of a retort and a separately

[1] J. S. C. I. 1896, 443.

[2] Petroleum, Asphalt and Natural Gas, Bulletin No. 14, Kansas City Testing Laboratory, 97.

[3] U. S. Patent 1,324,143, Dec 9, 1919.

[4] J. S. C. I. 1916, 1006; British Patent 10,679, July 22, 1915; Int. Conv. July 22, 1914.

heated retort extension. The material is heated in the main retort along with catalytic agents, such as iron oxide, nickel, etc., and in the presence of steam, hydrogen, or water gas. The volatilized oils are then heated in the extension. Condensers are used, and any part of the system may be subjected to pressure by means of a compressor with the necessary valves.

A novel method of deriving light mineral oils from heavier oils is suggested by **H. S. Maxim.**[1] He heats a mixture of heavy oil with finely divided zinc and slightly acidulated water to 300° to 420° C. (572°–788° F.) in a closed vessel which is rotated during the operation. The vessel is only partially filled with the liquid. After the desired transformation has been effected the lighter hydrocarbons are separated from the residual oil by distillation.

The Standard Oil Company [2] distills heavy hydrocarbons at 650° to 850° F. (343°–454° C.) under a pressure of 4 atmospheres or more, in the presence of extensive catalytic surfaces, which may consist of plates immersed in the liquid or of plates arranged in the vapor space. With this arrangement about two-thirds of the charge may be distilled off, the residue constituting an asphalt. The catalytic surfaces consist of steel, brass, or copper in the form of plates or gauze, or of mineral fibers such as asbestos or glass.

A process that is of interest in its bearing upon the action of organo-metallic compounds on petroleum is proposed by **MacAlpine** [3] in order, it appears, to prepare from a crude oil one which would be free from bad smelling compounds (possibly also to clarify the oil) rather than to produce gasoline. The organo-metallic compound used was a compound of manganese with acetylene prepared and applied as follows:

To a solution or emulsion composed of water containing the oxides, hydrates or carbonates of calcium, barium, magnesium, sodium, potassium, or ammonium is added a nearly saturated solution of the permanganates or manganates of calcium, barium, magnesium, sodium, potassium, or ammonium, and the mixture is treated with acetylene gas, which is either obtained in the ordinary way by the mutual decomposition of water and calcium carbide and passed into the mixture, or is produced directly in the mixture itself by introducing calcium carbide into it. For example, a solution in water of carbonate of sodium or carbonate of potash or a mixture of the two of a specific

[1] J. S. C. I. 1919, 567 A; British Patent 128,227, June 15, 1916.

[2] **R. E. Humphreys,** Chem. Abs. 1916, 1095; British Patent 21,273, Oct 20, 1914; Norwegian Patent 26,825, April 3, 1916. See also R. F. Humphries, U. S. Patent 1,122,003, 1914; **Standard Oil Co.,** British Patent 7541, Oct. 20, 1914.

[3] U. S. Patent 655,500, Aug. 7, 1900.

gravity of about 1.07 is taken. To this solution a saturated or nearly saturated solution in water of permanganate of potash is added, taking care not to add an excess. The point at which the addition of permanganate should be stopped can be determined by observing the color of the solution or emulsion. If an excess of permanganate is used, the color will be purplish red. The addition of the permanganate should be stopped as soon as a faint reddish tinge appears in the solution or emulsion. When the proper amount of permanganate has been added, the mixture is subjected to the action of acetylene gas intermittently for some time. The acetylene gas causes a precipitate containing manganese to be thrown down, which is then separated by filtration in the usual manner.

This is usually conducted at ordinary room temperature but to accelerate the process the temperature of the solutions may be slightly raised, and to increase the speed of absorption the acetylene gas may be introduced into the liquid mixture under pressure. Having thus prepared the acetylene compound of manganese, crude mineral oil is treated with the manganese compound in the following way: To one hundred gallons of oil five pounds of the manganese compound is added and the whole allowed to rest for several hours or days, with occasional agitation, or the mixture may be submitted to continual agitation for several hours. The mixture is settled, and when subsidence has taken place the oil is removed and distilled.

With impure petroleum or mineral oils an alkali may be used to assist the action of the manganese, and if such oils are very impure, then a mineral acid, ordinarily sulphuric acid, may be used When an alkali is used, the proportions are about as follows: For every ten pounds of the manganese compound (as above) from four to five pounds of caustic soda or caustic potash are mixed with the oil before the addition of the manganese compound, and in case acid is used for every ten pounds of the manganese compound four or five pounds of concentrated sulphuric acid diluted with about seven times its weight of water are taken. The acid may be mixed with the oil before the addition of the manganese compound.

In case acid is used after the action of the manganese compound upon the oil a sufficient quantity of alkali is added to neutralize an excess of acid. The salt thus formed and the excess of alkali are removed by washing the oil with water, after which the oil is distilled either with or without filtration or subsidence. In the operation of distillation it is advantageous to employ a complete or partial vacuum.
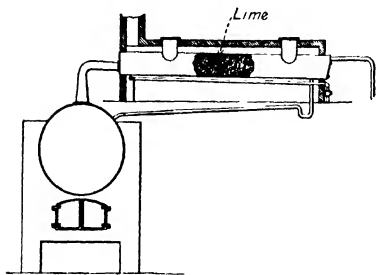
Fig. 166. — Fire still in series with lime-packed retort. Method of Koehler.

Koehler[1] passes the distillate from an ordinary fire still through a retort heated to 600° to 1000° F. (316°–538° C.). The retort is

[1] U. S. Patent 507,441, Oct. 24, 1893.

packed with lime. It is in the form of an elongated cylinder and is somewhat inclined, with its higher end connected to the goose neck of the still. A trapped pipe connects the lower end of the retort with the still, in order to reflux oils which condense in the retort. (See Fig. 166.) The primary object of the process is to assist in desulphurizing petroleum and its distillates. However, the temperature of the retort and lime would also cause cracking.

White [1] brings oil, which is preheated, into contact with lime (in the form of small pieces or lumps) which is heated in a retort. 550° to
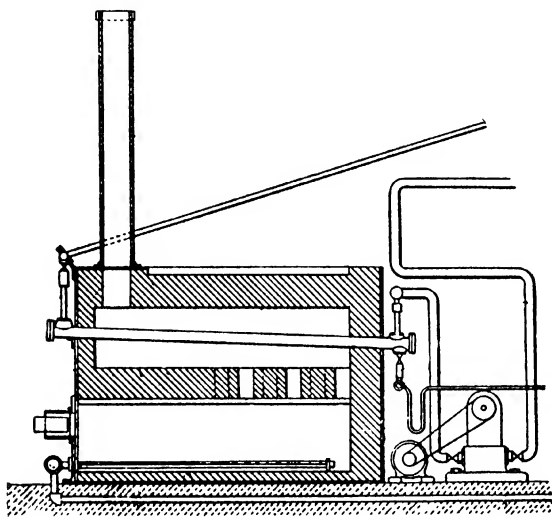
Fig. 167. — Apparatus proposed by White for use in decomposing oil in the presence of lime.

575° C. (1022°–1067° F.) is stated to be a very suitable temperature The oil or residue may be sprayed or trickled on to the lime or applied to it in a thin sheet or film.

The oil on coming into contact with the hot lime volatilizes, and the vapors of oil thus produced are absorbed into the lime, where it is stated they undergo molecular rearrangement, with consequent production of a large proportion of lower hydrocarbons of lower boiling point and lower flash point.

It has been found that if these vapors of lower hydrocarbons are allowed to remain in the sphere of reaction they undergo further decomposition, with the production of still lower boiling and flashing hydrocarbons, most of which are not condensable at ordinary temperature.

[1] Chem. Abs. 1915, 2310; J. S. C. I. 1915, 651; British Patent 5434, March 3, 1914; French Patent 477,771, Feb. 23, 1915; United States Patent 1,226,041, May 15, 1917.

In order to obviate this, a vacuum pump is attached to the retort or lir chamber.

The vapors from the lime retort or chamber are condensed and a liquid thus obtained containing a large proportion of hydrocarbons of low boiling point ai flash point. With crude paraffin oil, for example, a liquid containing from 20 25 per cent of hydrocarbon having a boiling point and flash point approximate those of gasoline, is claimed to be obtained by the above method.

The gasoline is removed by distillation and the residue again subjected to tl action of the heated lime.

Fig. 167 shows the apparatus used.

Herber [1] uses lime as an adjunct in producing low boiling hydro carbons. He has devised a horizontal cylindrical still which may 1 continuously rotated during the process of distillation, or crackin; and provides means for introducing fresh lime and steam or air into th heated oil. The apparatus is also built to withstand pressure in cas it is desired to crack under pressure. The rotatable feature is state to lessen the danger incident to the caking of carbonaceous deposits o the inside of the still.

M. E. Freudenheim [2] shows the effect of lime in decomposing ace tone. On passing acetone vapor over calcium hydroxide varying i temperature from 350° to 630° C. (662°–1166° F.) it was found tha with increasing temperature the gas mixture resulting showed increase percentage of carbon monoxide, methane and olefins and increase rate of evolution but decreasing percentage of hydrogen. The fo mation of methane indicates that acetone is an intermediate produc in the reaction between calcium acetate and calcium hydroxide whic gives calcium carbonate and methane. At 350° C. (662° F.) the gaseou products are almost exclusively methane and hydrogen. No satis factory reaction to account for the formation of hydrogen is suggested Carbon is deposited on the calcium hydroxide, increasing in amoun with rising temperature.

Day [3] adds sulphur, hydrogen sulphide, or other reducing sulphu compound to the mineral oil to prevent oxidation of the distillate b; sulphuric acid subsequently used in refining it and the oil is then sub jected to a cracking distillation under pressure. Hydrogen is mixe(with the oil vapors produced and the mixed vapors and gas are passe(through a catalytic mass, e.g., clay, iron, zinc, nickel, cobalt, platinum or palladium to further increase the yield of light oils. It is stated tha the addition of sulphur aids in the production of light hydrocarbons Ammonia and hydrogen sulphide are also used, as well as hydrogen

[1] U. S. Patent 1,183,457, May 16, 1916.
[2] Chem. Abs. 1918, 1641; J. Phys. Chem. 1918 (22), 184–93.
[3] J. S. C. I. 1917, 541; U. S. Patent 1,221,698, April 3, 1917.

In the form of apparatus described, the contact mass is contained in tubes immersed in the body of hot oil undergoing cracking treatment in the still. As examples of oils treated in the above manner, California, Texas and Mexican crudes are mentioned.

Brooks and **Humphrey** [1] state that petroleum oils, whether saturated, such as natural gasoline, or of the unsaturated type, e.g. cracked gasoline, deteriorate much more rapidly by oxidation on exposure to the air than portions of the same oils which have been freed from sulphur by treatment with lead or copper oxides or metallic sodium. It is possible that oxidation of the sulphur compounds causes a simultaneous oxidation of other constituents. This view is said to be supported by the fact that on heating petroleum residues with small amounts of sulphur, and shaking the mixture with natural gas, the product is much more fluid than that obtained by blowing air into the mixture.

Asphalts of exceptional hardness may be made by the combined action of air and sulphur. For example, on air-blowing a sample of residue from a Mexican oil, to which 8 per cent of sulphur has been added, for 31 hours at 220° to 230° C. (428°-446° F.), the resulting product had a flowing point of 185° C. (365° F.) and a penetration of 7 mm. at 25° C. (77° F.). Another product made from the same residue, with the addition of 12 per cent of sulphur, had a flowing point of 200° C. (392° F.) and a penetration at 25° C. (77° F.) of 5 mm. (100 grm. weight, No. 2 needle, 10 secs). In practice, products as hard as this are seldom required, but the addition of 3 to 5 per cent of sulphur has a pronounced effect in producing hard asphalts in a much shorter time (e.g., 14 hours as against 96 hours) than can be obtained by air-blowing residues to which sulphur has not been added. Hence, residues relatively rich in sulphur will yield hard asphalts in less time, when blown with air, than those poor in sulphur.

The action of sulphur on naphthenes has been investigated by **W. Friemann.** [2]

It has been found that fractional distillation in vacuo of the product of the action of sulphur on cyclohexane under pressure gave a first fraction, considered to be cyclohexadiene, giving m-dinitrobenzene with a nitrating mixture, a second fraction containing thiophenol, considered to be formed from cyclohexene via cyclohexadiene, and a residue containing phenyl sulphide. A thiocresol was isolated from the products of the action of sulphur on methylcyclohexane under pressure. In the case of dimethylcyclohexane (octonaphthane), in addition to the formation of hydroxylenes and thioxylenol, xylene itself is produced at one stage and gives mm-dimethyldibenzyl. It follows, it is said, that the presence of aromatic hydrocarbons in petroleum can scarcely be due to the action of sulphur on naphthenes under pressure, as no sample has yet been found to contain thiophenol or a homologous aromatic mercaptan.

[1] J. S. C. I. 1917, 997; J. Ind. Eng. Chem. 1917, 9, 746–748.

[2] J. S. C. I. 1917, 204; Petroleum 1916 [9], 978–982; Z. Angew. Chem. 1916 [29], Ref. 531.

Melamid and **Grotzinger** [1] treat tar oils, tars, and tar derivatives, for the production of light hydrocarbons, suitable to use as motor fuel, by distilling with phosphoric acid (H_3PO_4) in the presence of indifferent gases or vapors. Nitrogen, steam, hydrogen and air are mentioned as suitable indifferent gases. The phosphoric acid may be introduced continually during the operation, or may be added initially, and is maintained in a finely divided condition by stirring. If, for example, tar from the Freiburger Gasanstalt is distilled without phosphoric acid, only 6.49 per cent of the constituents, of specific gravity 0.950, boiling below 200° C., (392° F.) resulted, while the same amount of tar, distilled with 25 kilos. phosphoric acid, in continuous operation and in the presence of an indifferent gas or vapor, yielded 30.05 per cent of a product of specific gravity 0.897 and boiling below 200° C. The amount of pitch in the first case amounted to 44.3 per cent and in the last case only 22.05 per cent. When the oils obtained under the specified conditions are treated again in the same manner, they are again cracked, yielding hydrocarbons with still lower specific gravity of 0.860 and boiling below 120° C. (248° F.) The distillate boiling below 120° C. is said to serve well as a substitute for benzine in automobiles with the usual carbureter, to be also about 12 per cent richer than benzine of specific gravity 0.720, and to form exhaust gases having a less disagreeable odor.

[1] Chem. Abs. 1914, 1344; 1915, 963 and 712; 1916, 1927; British Patents 1489 and 1490, Jan. 29, 1915; German Patents 276,775, Aug. 19, 1913, and 278,192, Aug. 21, 1913.

CHAPTER XX

CRACKING BY MEANS OF FUSED BATHS

Many investigators have realized that overheating an oil has a tendency to decompose it into fixed gas and carbon. For example, by forcing oil through red hot tubes it is possible almost completely to break the oil up into fixed carbon and gas without the formation of any naphtha, if the vapors remain long enough in contact with the heated surfaces. With direct firing, overheating is sometimes difficult to avoid. With this in view many processes have been proposed for maintaining a more uniform temperature by means of fused baths of metals or salts.

Where the fused material is contained in a still or retort one of the advantages thereby secured consists in the fact that the customary carbon deposit tends to float on top of the melted substance (lead, for example) instead of becoming attached to the bottom of the still.

A. Duchesne [1] makes oil gas by discharging oil directly into melted lead. It is claimed that this method is not attended with the overheating difficulties encountered in passing oil through heated tubes and retorts.

L. Stevens [2] proposes blowing a mixture of oil and steam through molten asphalt heated above 600° F. (316° C.) in order simultaneously to distill and desulphurize oil. It is noted that the action of the steam oxidizes the sulphur. The mixed steam and oil vapors then pass into a series of air and water condensers and products of different gravity are obtained by fractional condensation in a manner similar to the operation of tower stills.

F. J. Carman [3] desulphurizes oils by forcing them through molten lead (see Fig. 168). It is said the sulphur of the oils is converted into lead sulphide. By blowing air through the mass at the end of a " run," the sulphur of the lead sulphide is observed to be oxidized to sulphur dioxide and to pass off as such, leaving a residue of lead oxide which, during the subsequent action of the petroleum vapors, is reduced to metallic lead.

[1] U. S. Patent 179,005, June 20, 1876.
[2] U. S. Patent 414,601, Nov. 5, 1889.
[3] U. S. Patent 501,988, July 25, 1893.

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A. Seigle [1] passes heavy oils through preheating and vaporizing chambers heated by a fused bath and then through similar cracking chambers filled with contact refractory material. Here decomposition takes place and light oils are formed. The decomposing chambers are also heated externally by a fused bath.

In Figures 169 and 170, G represents a pipe leading from a reservoir, containing the crude hydrocarbon, to a series of vaporizing chambers. The pipe G is controlled by a meter or regulator H by means of which the flow of hydrocarbon through the pipe G to the vaporizing chambers may be regulated at will. The vaporizing chambers I, I, and I are arranged, as shown, that is, each chamber I is separated into six compartments by a series of staggered partitions I^2, Fig. 170,
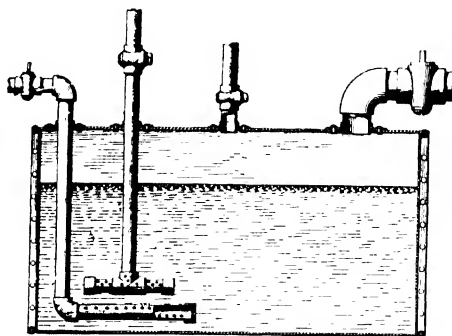
Fig. 168. — Apparatus employed by Carman.

the heated hydrocarbon passing into each of these compartments successively, as indicated by the arrows. The vaporizing chambers I, I, and I are connected together in series, so that the heated heavy hydrocarbon is obliged to successively traverse each of the vaporizing chambers before it can enter by the pipe K into a series of the heating chambers J. These heating chambers J are arranged as shown in Fig. 169, each chamber J being provided with a separate inlet from the pipe K and with a separate outlet. These chambers J, unlike the vaporizing chambers I, are filled with obstructive or inert matter, such as iron chips, pumice stone, or the like, through which the heated hydrocarbon vapors must percolate before they escape into the outlet pipe N.

At the bottom of each heating chamber J is an open space in which the vapors collect, and leading to this space in each chamber J is a branch pipe L, to remove the vapors through the pipe L from the chambers J. The outlet pipe N conducts the highly heated hydrocarbon vapors to a condenser.

The heating chambers J and vaporizing chambers I are suspended in a bath of molten lead contained in a vat V. This vat is permeated by a series of heating or combustion flues X, which convey hot gases from a spray-like burner or gasifier Y through the molten metal to maintain it at a uniform temperature. The gases pass from the flues X to a flue Z, and from thence to a chimney.

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[1] U. S. Patent 567,752, Sept. 15, 1896; British Patent 23,235; Dec, 4, 1895; French Patent No. 252,068, Nov. 29, 1895.

In the bath of molten metal is plunged a pyrometer a, connected by means of a bent lever b to the inlet to the burner Y. The inlet is controlled or automatically regulated by the pyrometer a and lever b in such a manner as that variations in the temperature of the molten bath will increase or decrease the size of the jet of combustible liquid, such as heavy hydrocarbon, delivered to the burner
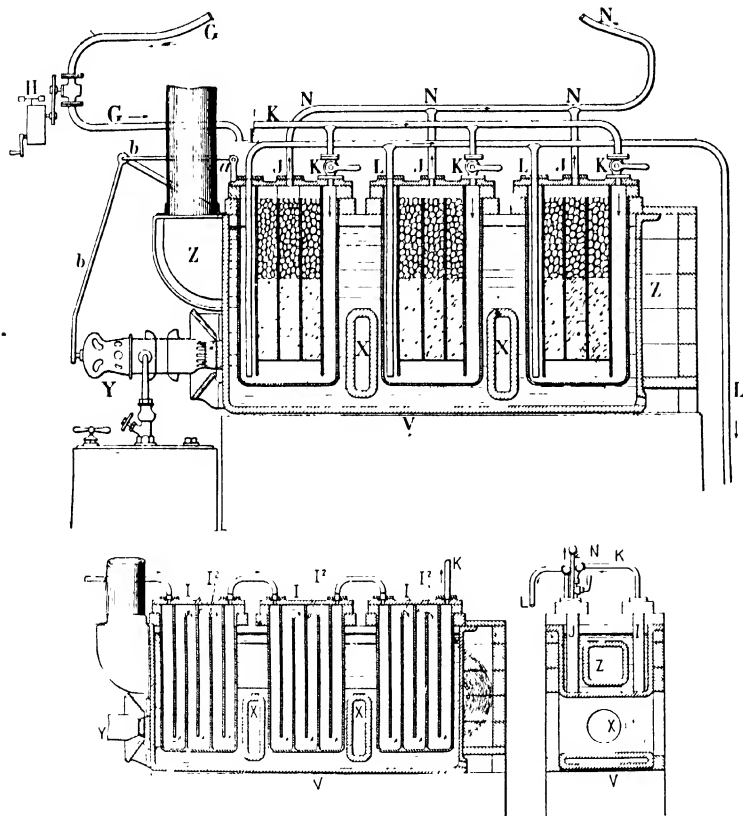
Figs. 169 and 170. — Apparatus recommended by A Seigle.

Y. As shown in the drawings, both the heating chambers J and vaporizing chambers I are immersed in the same bath of molten metal, but it will be found advisable in practice, it is stated, to immerse each in separate baths in order to heat the two chambers to the different temperatures which is necessary.

• The apparatus thus includes the following essentials: first, a bath of molten lead or similar material to maintain the heating chambers at a constant temperature, and, second, the use in the apparatus of heating chambers and vaporizing chambers, the vapors circulating through all the chambers previous to their treatment in the heating chambers.

The operation is as follows: The burner Y is first lighted and the metallic bath fused and brought to required temperature. The crude hydrocarbon is then delivered from the pipe G to the chambers I in which the hydrocarbons are heated and a certain portion vaporized, and from the chambers I the hydrocarbons are conducted to the chambers J, in which the vapors are both separated and super-heated. The vapors from the chambers J are drawn off through the pipe N to a reservoir or condenser.

S. E. Kelsey [1] decomposes heavy oils under pressure in a retort which contains a mass of fused metal or alloy and is also packed with nonfusible metallic packing (Fig. 171). A is the retort, containing a mass of fused metal. A pump forces oil to the bottom of the retort, the oil is distilled and partly decomposed by contact with the fused metal and the non-fused metallic packing. A check valve on the vapor line maintains pressure in the retort. The metallic packing is used to secure as large as possible an interior heating surface. Heavy residuum collects on the surface of the fused

Fig. 171. — Converter proposed by Kelsey.

material and is drawn off through pipe B.

P. Danckwardt [2] circulates molten material into and out of a pressure retort and sprays a layer of heavy oil continuously onto the mass of molten material (lead, or sodium hydroxide) in the retort. A loaded valve is placed between the still and condensers.

In Fig. 172, A is the coil for heating the circulating molten material and B is the still. Molten lead, for example, is introduced into the still through pipe G' nearly up to the level of pipe G and through pipe F until the coil A is nearly filled. Cold water jackets then are used to plug the filling lines. Suction pump C is now operated and circulates the molten material. When the proper temperature is attained in the still, the oil to be cracked is pumped in slowly from the storage tank D.

[1] U. S. Patent 1,092,366, April 7, 1914.
[2] Chem. Abs. 1915, 1994; U. S. Patent 1,141,529, June 1, 1915.

Oil is pumped in so slowly that only a thin layer of heavy residue is allowed to collect on the surface of the melted metal. Vapors expand through the throttling valve and are condensed.

Examples. Results are given on an oil with a rather heavy base, which gave by common fractional distillation at atmospheric pressure 7 per cent light hydrocarbons of a boiling point up to 150° C. (302° F.), 32 per cent of a boiling point up to 250° C. (482° F.) and the rest of a boiling point above 250° C. (482° F.). When this oil was subjected to
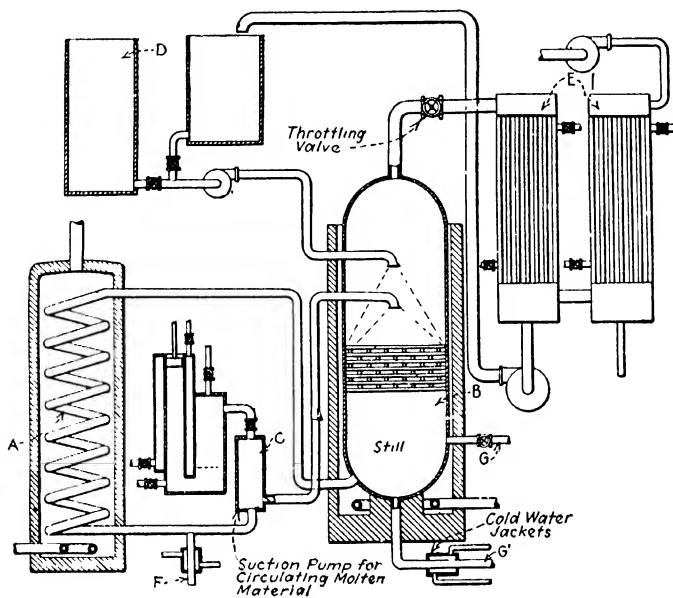
Fig. 172. — Danckwardt's continuous still.

cracking under a pressure of about 125 pounds per square inch and at a temperature of about 400° C. (752° F.), it gave in one distillation: 65 per cent naphtha, boiling point up to 150° C. (302° F.), 20 per cent of a boiling point up to 250° C. (482° F.), 10 per cent of a boiling point above 250° C. (482° F.), containing some carbon and 5 per cent fixed gas. By returning the fractions boiling at 250° C. (482° F.) and that boiling above 250° C. (482° F.) there was obtained 15 per cent more naphtha boiling point up to 150° C. (302° F.) and 7 per cent of a boiling point up to 250° C. (482° F.), the rest of a boiling point point above 250° C. (482° F.). A third operation increased, it is said, the total of naphtha by only 5 per cent. In practice these undecomposed fractions are generally not worked up for themselves, and are best added

to fresh oil in order to always keep the composition of the oil entering the still as uniform as possible unless they are cut out of the process altogether and worked up for the production of special oils.

F. Pfeifer [1] makes oil gas by passing oil through a molten metal. The carbon which ordinarily forms and gives difficulty floats on the surface of the liquid in the form of an amorphous powder.

J. Nelson [2] forces hydrocarbon oil or vapor through a bath of molten metal. For working at moderate temperatures, molten lead is a suitable substance; for higher temperatures, metals or alloys of higher melting point may be used. The extent of cracking is controlled by varying the depth at which the oil or vapor is delivered below the level of the liquid. If the hydrocarbon contains tarry matter, or substances which cannot be volatilized, it is distilled from an auxiliary vessel, and the distillate or vapors then subjected to the cracking process. The passage of the vapors through the liquid keeps it thoroughly agitated, thus maintaining a uniform temperature throughout the mass and preventing accumulation of carbonaceous material. A form of apparatus for the process consists of a vertical cast-iron cylinder about 2 feet 6 inches high and $2\frac{1}{2}$ inches internal diameter, heated at its lower end, and provided at the upper end with a lateral exit pipe and a gas tight cover through which passes an adjustable inlet pipe, the lower end of which is immersed in a quantity of molten lead. Kerosene of specific gravity 0.803 after one treatment in this apparatus, the lead being maintained at about 700° C. (1292° F.) and the inlet pipe dipping 4 inches below the surface of the lead, yields, it is said, about 20 per cent of light gasoline of specific gravity 0.757 and boiling at or below 160° C. (320° F.).

A. A. Wells [3] vaporizes oil and passes it into a bath of violently agitated molten lead maintained at a temperature of 480° to 540° C. (896°–1004° F.). Gases produced by the cracking are collected and returned to the metal bath and burned within a pipe filled with refractory material in the bath.

An expedient adopted by **J. H. Adams** [4] is that of using a layer of molten lead on the bottom of a cracking still. Oil to be cracked is passed through a preheating coil and then to a shallow layer of oil upon the highly heated bottom of a cracking still, where it is separated from

[1] Chem. Abs. 1917, 3118; Canadian Patent 175,601, March 6, 1917.

[2] J. S. C. I. 1918, 457A; British Patent 116,304, March 13, 1917. Appl. No. 3668 of 1917.

[3] Chem. Abs. 1916, 2144; U. S. Patent 1,187,874, June 20, 1916.

[4] J. S. C. I. 1920, 7 A; Chem. Abs. 1920, 221; U. S. Patents 1,320,726 and 1,320,727, Nov. 4, 1919; see also U. S. Patent 1,320,354.

the bottom of the latter by a layer of molten lead. This shallow layer of oil is separated from the main bulk of oil in the cracking chamber by a constriction of the walls of the chamber a short distance above its bottom. The temperature of the plate covered by the molten lead may be from a cherry-red to a much higher heat. The bulk of oil in the cracking chamber is held at a constant level to supply pressure upon the oil in contact with the molten metal at the bottom of the chamber. Superheated steam may be forced into the oil in the cracking zone.

Roth and **Venturino** [1] describe a method for cracking crude petroleum and the heavier products of petroleum including the burning oils, gas oils, and lubricating oils, to yield naphtha. It consists in distilling off
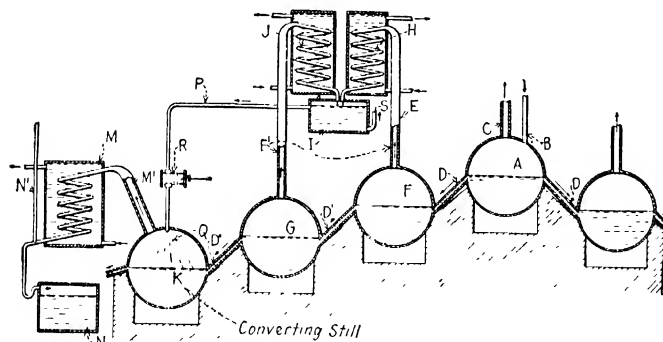
Fig. 173. — Proposal of Roth and Venturino.

the lighter products, that is, light and heavy naphtha, in crude oil, when this is used as the immediate raw material, and then distilling off the heavier fractions. These heavier fractions are then compressed and sprayed onto highly heated asphalt in a " converting still." This breaks the heavier products down partly into naphtha. The asphalt may be obtained, as shown in Fig. 173, from the continuous distillation of the same crude oil from which the naphtha and cracking stock are produced.

The heavy petroleum products fall, either in a liquid condition or atomized, upon a mass of residues of petroleum, asphalt, or oils, heated to a temperature higher than the boiling point of the hydrocarbons which are to be converted. The vapors and gases generated on the contact of the atomized heavy hydrocarbons with the heated mass are then condensed.

The apparatus consists of a series of stills, arranged on graduated levels and communicating with each other by means of connecting pipes which connect every

[1] Chem. Abs. 1917, 2541; 1917, 300; U. S. Patents 1,208,378, and 1,208,214, Dec. 12, 1916; British Patent 106,012, Sept. 20, 1916. See also Venturino, British Patent 12,570, Sept. 1, 1915.

two successive stills at about the middle of their height. In order that the conversion or transformation may take place continuously, it is preferable to arrange a double series of stills consisting of two symmetrical halves, of which only one is illustrated.

The still A is provided with a pipe B for the admission of the petroleum and with a pipe C for the discharge of the vapors of distillation generated in the interior of the still. The still communicates at about the middle of its height, by means of an inclined pipe D with another still F similarly provided with a discharge pipe E for the vapors of distillation. The still F communicates with the still G arranged at a lower level than the former, through an inclined pipe which connects them at about the middle of their respective heights. The distilling pipe E of the still F ends in a coil H, arranged within a refrigerating tank, in which a circulation of water is maintained. The still G is provided also with a pipe for the discharge of the vapors of distillation generated and this pipe ends in a coil J. The coil J as well as the coil H, on issuing from the refrigerating tank, discharges at the upper part of the separating vessel I.

The still G communicates with a still K. This latter still K is the one in which the conversion is performed. This converting still is provided with a discharge pipe M' for the vapors of distillation, ending in a coil arranged within a refrigerating tank M. This coil terminates in a trap and discharges into a reservoir N in which the condensed converted products are collected.

The separating vessel I is provided at the side, near the top, with a discharge pipe P which discharges from this vessel the heavy or middle oils. The pipe P is arranged with a compressor R. The heavy hydrocarbons, after being compressed, pass into the interior of the still K through an atomizer Q.

The separating vessel I works automatically. This vessel consists of a casing provided at the top with a pipe for the escape of the gases, and at one of its sides, near the bottom, with pipe S which bends upward and the length of which has been calculated so as to keep water inside the vessel or reservoir always at the same level. In this manner, when the condensed vapors fall into the vessel through the ends of the coils, they fill it above the level of the water, and in the event of any water or impurities being carried along by the vapors, the level of the water in the vessel cannot rise, as it escapes through the pipe S.

In the boiler or still A the temperature is maintained at a sufficient height for distilling the light hydrocarbons of the petroleum which is fed into the still continuously by means of the pipe B. This temperature is about $200°$ C. ($392°$ F.) which is sufficient for distilling away all the lighter hydrocarbons, down to benzine inclusive. The vapors of distillation issue from this still by the pipe C and are condensed. When the level in the still reaches that of the discharge pipe D, the petroleum, already deprived of naphtha, passes to the still F in which a sufficiently high temperature is maintained for distilling the kerosenes and the proportion of oils which may be desired in this still, for example, up to 70 per cent of the entire volume of petroleum introduced into the still A. When the level of the liquid in the still F reaches that of the discharge pipe D', it passes into still G where the residues will even yet distill off a small quantity of oils and where the temperature should be slightly lower, from $10°$ to $20°$ C. ($18°$–$36°$ F.), approximately. This slight lowering of the temperature is in order to prevent the mass of residues from boiling when these enter by the pipe D'' into the converting still K, after having filled the still G to the level of the outlet pipe of the latter. The vapors of distillation which escape from the stills F and G by the pipes E and E' are condensed in the coils H and J, and the resulting heavy products collected in the

separating vessel I, which separates the petroleum or products obtained from it from the water or impurities which may have been carried along during distillation and the gases which may not have been condensed. The hydrocarbons contained in the separating vessel I pass from it by the pipe P to the compressor R and finally to the atomizer Q and from there they are injected into the converting still K in the form of a fine spray which falls upon the heated mass of residues contained in that still. The vapors of distillation pass out by the pipe M' to the coil M. It is considered advisable to keep the temperature within the refrigerating tank exceedingly low, for the purpose of condensing the petroleum ether which may be carried along by the gases. The coil is connected to a trap before its entrance into the vessel N. The main object of the trap is to prevent the entrance into the vessel of the gases and petroleum ether, which are allowed to escape to the outer air by the tube N'. After the vapors have been condensed within the coil M the resulting liquid passes to the reservoir N.

It may happen that on certain occasions kerosenes and other oils are found in the reservoir N in which case they are submitted to fractional distillation, and introduced again into the converting still by means of the atomizer Q. When there is need of preserving the kerosenes naturally contained in the petroleum or even in increasing their proportion, one of the following two methods may be 'used:

(1) Within the still A, a temperature should be maintained sufficient to distill besides the light hydrocarbons, also the kerosene which may be desired; for instance, a temperature up to about 270° C. (518° F.) is used and the subsequent procedure followed as indicated in connection with the other stills. (2) Between the stills A and F another still, not shown, may be inserted, for distilling off the kerosenes, and the vapors of this distillation will then be collected and condensed separately. As regards the remainder of the operations, the process is the same as that which has been described above.

In order to obtain a continuous conversion, a double series or battery of stills is used, and in the pipes D are arranged valves by means of which the operation may be transferred from one side of the double battery or series to the other, in order that the operation of one of the sides may be suspended to effect the discharge and cleaning of the stills.

R. Fleming [1] heats heavy petroleum products such as heavy fuel oils or heavy pitchy residues with hydrocarbon products of lower boiling point at temperatures in excess of 350° C. in order to effect such conversions that an increased yield of gasoline may be derived from the resulting mixture on distillation. A pitchy residue of 12° to 20° Bé. may for this purpose be maintained at approximately its boiling point under the temperature used (about 400° C. (752° F.) with a continuous supply and circulation of the liquid in the apparatus under a pressure of 75 to 100 lbs. per sq. in. Kerosene distillate of about '43° Bé. or heavier and boiling above 180° C. (356° F.) is continuously 'supplied through a perforated pipe into the lower portion of the main body of the heated liquid in quantity just sufficient to maintain the pressure. From the mixture thus constituted an oil distills over having

[1] Chem. Abs. 1920, 465; U. S. Patent 1,324,766, Dec. 9, 1919.

light and heavy fractions, which is found to yield a large amount of gasoline when fractionated. Free carbon is deposited in the bottom of the apparatus and is drawn off as formed; so that the process may be operated continuously. When oils boiling above $325°$ C. ($617°$ F.) are used a higher boiling solvent menstruum somewhat heavier than $12°$ to $20°$ Bé. may be used. The use of the heavier solvent maintains the necessary high temperature for effecting conversion and also itself takes part in the conversion reactions and increases the gasoline fraction which may finally be derived from the resulting oil mixture. If coal-tar distillates are employed in the method, a product is obtained which is claimed to yield large amounts of benzol, toluol and xylol. No steam, catalysts or desulphurizing agents are employed in the process.
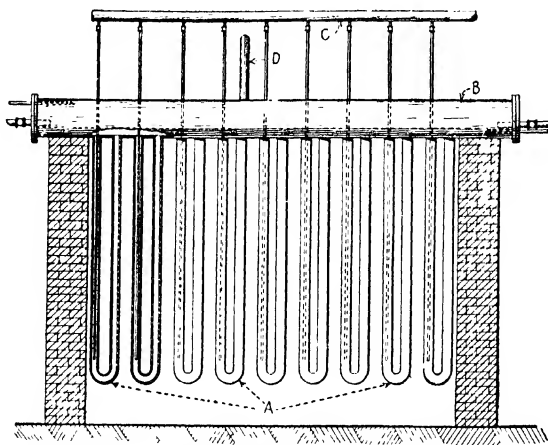
Fig. 174. — Fused lead method of Andrews and Averill.

The distillate to be converted is injected into the body of heavier oil below ascending tubes, so that globules of vapor ascend through a column of highly heated heavier oil and are thereby rapidly brought to the temperature necessary to effect conversion. Yields as high as about 65 per cent of gasoline are stated to be obtainable by this method from kerosene distillate of $43°$ Bé.

An interesting adaptation of the fused-bath method is described by **Andrews** and **Averill**.[1] A number of U-shaped tubes (A, Fig. 174) containing molten lead are suspended from a horizontal header, B, also containing molten lead. From an oil supply header C, oil tubes extend

[1] U. S. Patent 1,312,467, Aug. 5, 1919. See also Andrews and Averill (U. S. Patent 1,329,739, Feb. 3, 1920; and U. S. Patent 1,312,467, Aug. 5, 1919).

down into one leg of each of the U-tubes. Vapors collecting in B are discharged through D to condensers. The rapid evolution of vapor caused by contact of hot lead and oil near the bottom of one leg of each U-tube causes a rapid upward movement of lead and oil vapor in that leg and a corresponding downward movement of lead in the other leg of the U-tube. Thus a circulation is generated and maintained that assists in preventing carbon deposit. The carbon collects on the surface of the lead in the header B. A uniform vapor pressure is sustained, for example, 75 pounds, with the assistance of steam. Condensation takes place under pressure.[1]

[1] See also pages 158, 202, 239, 248 for further examples of the use of fused baths.

CHAPTER XXI

CRACKING WITH THE AID OF INTERNAL HEAT

By " internal heat " is meant heat derived from a combustion, restricted or complete, or both, of a part of the hydrocarbon material being treated.

It has long been the ambition of petroleum technologists to decompose heavy oils by means of direct heat, i.e., without the interposition of any containing walls or diaphragms between the oil and the source of heat. To burn, partly or completely, a portion of the oil being cracked, in the interior of, or on the surface of, that oil itself represents, indeed, a large heat conservation — provided the cracking stock is a low grade oil, such as fuel oil. Many attempts have been made to commercialize the method.

One important feature of this general method is the elimination, even the direct *utilization*, of the carbon deposit, which is a source of so much trouble even in processes that are being successfully practiced at the present time. One of the ideas is to burn the carbon deposit as fast as it forms. Aside from the purpose of utilizing heat directly, in this manner, for the sake of obtaining *heat* energy, there is also the *chemical* effect of oxidation, meaning restricted oxidation. A good example of this is the oxidation of naphthenic hydrocarbons into aromatic hydrocarbons, i.e., the dehydrogenation of naphthenes and hydroaromatic or alicyclic hydrocarbons.

M. H. Strong [1] decomposes oil in retorts to make gas, in the presence of refractory contact material. A blast of air is then used to burn the resulting deposit of carbon, the heat from this combustion serving to heat the contact material. This stored-up heat is then utilized to decompose a fresh portion of oil.

Strache and **Porges** [2] conduct vapors of heavy hydrocarbons, for example, gas oil, mixed with steam over an oxygen transferrer at a comparatively low temperature, thus giving, it is said, a large output of benzine or gasoline, having a low boiling point, and but small quantities of gas, the object being to reduce the gas production to a minimum. The oxygen transferrer is an oxide of a suitable metal, for example,

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[1] U. S. Patent 179,369, June 27, 1876.
[2] J. S. C. I. 1915, 826; U. S. Patent 1,205,578, Nov. 21, 1916.

iron oxide, lead oxide, cerium oxide, or pyrolusite. The regeneration of the substance, which becomes more or less mixed or coated with carbon during the process, is effected by conducting oxygen or air through the heated catalyzer. This coating of carbon is stated to be practically negligible when the proper supply of steam is maintained and the temperature kept low. The cracking smell is also reduced when care is taken to promptly reoxidize the oxygen transferrer as soon as the yield of light oils begins to decrease. B is a distilling vessel (Fig. 175) containing gas oil; the latter having a density of 0.8 to 1.0, and beginning to boil at 150° C. (302° F.).

Steam is conducted into the vessel B, and the mixed steam and heavy hydrocarbon vapor pass through a valve to the retorts, A, filled with a substance capable of transferring oxygen to the oil. The retorts A are heated by gas jets. Distil-
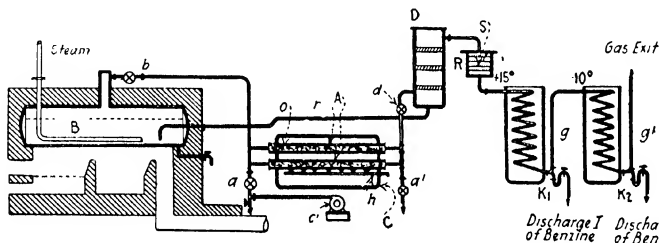
Fig. 175. — Method of Strache and Porges.

lation with steam takes place at a temperature between 140° C. (284° F) at the beginning of the operation and is gradually raised to 300° C (572° F.). The decomposition in the retorts A takes place when the temperature of the retorts reaches about 600° C. (1112° F.). The quantity of the oxygen transferrer used is dependent upon the quantity of oil to be treated in a unit of time; for example, if 100 kg. of oil is to be converted into gasoline in one hour, 100 kg. of catalyzer (iron oxide) will be required.

The products of the reaction pass from the retorts A filled with metal oxide O to a dephlegmator D from which the heavier constituents are returned by a pipe r to the vaporizer B, while the lighter constituents or gaseous products pass to a purifier R provided with a mass S containing lead oxide and an alkali or an alkaline earth, by which the smell due to cracking is removed. The light hydrocarbon is condensed in a cooler K_1 at a temperature of about + 15° C. (59° F.), and gases are then conducted to a second cooler K_2 and cooled to a temperature of about − 10° C.; the uncondensed gases issue from the pipe q_1. These gases either escape or are used for heating the vaporizer and retorts, or may be compressed into containers for future use.

After about six hours of operation, the gasoline or benzine flowing from the cooler K_1 begins to show an increasing percentage of hydrocarbons having a boiling point of over 150° C. (302° F.). This is an indication that the transformation of the heavy to the lighter hydro-

carbons is not progressing satisfactorily, and that the oxygen transferrer requires regeneration. Valves b and d are now closed and valves a and a_1 opened, the valve a admitting air or oxygen, which is energetically blown through the heated retorts A, effecting the combustion of the deposited carbon and the reoxidation and the oxidation to a higher stage of the oxygen transferrer. The products of combustion leave the retorts and pass out through the valve a_1, where the nature of the gas or flame of the ignited gas, or the absence of flame, will determine when the regeneration has been completed. Valves a and a_1 are then closed and valves b and d again opened, and the process continued as before. By regenerating the oxygen transferrer in this manner its original effectiveness is not only restored, but after repeated regeneration the transferrer is said to become more effective than when first used, probably due to the opening up of its surfaces, so that the process can be carried out at a lower temperature (with an iron oxide as oxygen transferrer, between 500° C. (932° F.) and 600° (1112° F.)) and the quantity of uncondensable gas is considerably reduced, while the product desired, namely gasoline, or benzine, is increased in volume.[1]

Porges and **Strache** [2] make oil gas, suitable for carbureting water gas, and containing light hydrocarbons, such as gasoline, benzol, and toluol from mineral oil, tar oils, brown coal tar, gas tar, etc., by cracking at temperatures below 700° C. (1292° F.) separating the light hydrocarbons and gas from the products, and returning the residue for further treatment in admixture with a fresh portion of the raw material. A temperature of 500° to 600° C. (932°–1112° F.) is preferably used. When a catalyst such as ferric oxide is employed, the temperature is raised as the proportion of residue increases.

C. F. Thumm [3] atomizes heavy oil with compressed air, or air and steam, and passes the atomized mixture through a hot tube heated by direct heat in a furnace. The mixture is then subjected to condensation at successively decreasing temperatures, the final cooling temperatures used being at or below the freezing point of water.

A. S. Ramage [4] passes heavy paraffin oils over heated reducible metallic oxides. Oxidation takes place with the production of olefins, terpenes, and aromatic hydrocarbons, a large percentage of which is reported to consist of low boiling oils.

[1] **Porges** and **Stransky**, Chem. Abs. 1915, 2814; Italian Patent 142,453, May 30, 1914. See also **Porges, Stransky** and **Strache**, J. S. C. I. 1915, 826; Chem. Abs. 1915, 3358; British Patent 11,420, May 8, 1914.

[2] Chem. Abs. 1918, 994; British Patent 112,420, October 4, 1917.

[3] U. S. Patent 389,988, Sept. 25, 1888.

[4] Canadian Chem. Jour. 1918 (2), 192–5; U. S. Patent, 1,224,787, May 1, 1917.

Hydrocarbons are transformed, by restricted oxidation, by means of a suitable reducible metallic oxide into other hydrocarbons containing proportionately less hydrogen, water being produced in the reaction. Paraffin hydrocarbons are stated to be transformed into olefins, for example pentane into amylene, or into terpenes such as pinene and limonene; or into aromatic hydrocarbons of the benzene type. Presumably the formation of olefins, terpenes and aromatic hydrocarbons represents the successive stages in the restricted oxidation of a paraffin, so that each of these groups may be regarded as derived from the preceding group richer in hydrogen, by removal of a portion only of this hydrogen. On this assumption some of the reactions involved might be thus expressed, using generalized formulae:

(1) Conversion of a paraffin into an olefin

$$C_nH_{2n+2} + O = C_nH_{2n} + H_2O$$
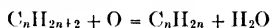
(2) Conversion of an olefin into a terpene

$$C_nH_{2n} + O_2 = C_nH_{2n-4} + 2H_2O$$
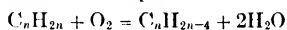
(3) Conversion of a terpene into an aromatic hydrocarbon

$$C_nH_{2n-4} + O = C_nH_{2n-6} + H_2O$$
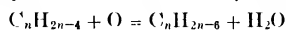
It is stated, however, that the production of an aromatic hydrocarbon may be regarded as taking place directly by the restricted oxidation of a paraffin or an olefin, the intermediate reaction stages, if such there be, being disregarded; thus:

(4) Conversion of a paraffin into an aromatic body

$$C_nH_{2n+2} + 4O = C_nH_{2n-6} + 4H_2O \text{ or}$$
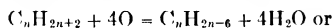
(5) Conversion of an olefin into an aromatic body

$$C_nH_{2n} + 3O = C_nH_{2n-6} + 3H_2O.$$
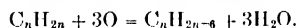
(6) Similarly an equation may be written to represent the direct transformation of a paraffin into a terpene:

$$C_nH_{2n+2} + 3O = C_nH_{2n-4} + 3H_2O.$$
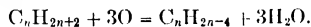
In practice, the belief is expressed that the reaction does in fact occur in successive stages, inasmuch as the reaction products are said to contain representatives of most or all of the above-mentioned groups (olefins, terpenes and aromatic bodies).

There occurs in each case an oxidation of a portion only of the hydrogen component of the hydrocarbon, whereby a hydrocarbon of any given series (paraffin, olefin or terpene) is transformed or converted into a hydrocarbon or hydrocarbons of a series relatively poorer in hydrogen. Another product of this restricted oxidation is in each case water, and the amount of water produced, relative to the amount of hydrocarbon treated, is said to be an index of the extent to which the oxidation has progressed. Therefore the reaction is controlled by collecting the water of oxidation and determining its quantity.

A hydrocarbon, or usually a mixture of hydrocarbons, is subjected to restricted oxidation by a reducible metallic oxide under conditions of temperature and time which are regulated according to the oxide used, the character of the hydrocarbon to be transformed, and the nature of the products desired. The hydrocarbon, in a state of vapor, passes over or through a bed of reducible oxide contained in a tube or retort. The temperature within the tube is maintained at a point which is sufficient for the reduction of the oxide in question, and the time and temperature are regulated with reference to the yield of water in order to produce the particular hydrocarbon mixture desired.

Using ferric oxide (Fe_2O_3) a temperature range of 580° to 750° C. (1076°–1382° F.) is suitable. Within these limits, provided a sufficient excess of iron oxide be present, there is reported to be no appreciable separation of carbon. At higher temperatures, or if the reduction of the oxide is carried too far, cracking sets in and the reduced metal contains carbon. Ferric oxide employed as above undergoes successive reduction to Fe_3O_4, FeO and metal. For the best operating conditions it is preferred to stop the treatment when the charge in the retort has been largely reduced to ferrous oxide FeO, containing some iron. The reduced charge may be regenerated by blasting it with steam while maintaining a temperature of approximately 750° C. (1382° F.) without removing it from the tubes. In the course of this regeneration hydrogen is produced. In case hydrogen is not desired the regeneration may be accomplished by means of air or a mixture of air and steam.

Between the approximate temperature limits (580°–750° C.) (1076°–1382° F.) a careful adjustment between the temperature of the oxide and the boiling point of the hydrocarbon to be transformed is necessary. Thus for a hydrocarbon fraction boiling between 150° and 200° C. (302°–392° F.) the lower temperature ranges 580° to 625° C. (1076°–1157° F.) are used; whereas for a fraction boiling between 250° and 300° C. (482°–572° F.) the higher temperature ranges, say between 700° and 750° C. (1292°–1382° F.) are used, the intermediate fractions requiring intermediate temperatures for the best results. In practice the boiling point of the material under treatment is observed and the temperature of the oxide regulated accordingly: For example, when treating an oil fraction of which the boiling point rises progressively, the temperature of the oxide is progressively increased.

Example: The material treated was a complex hydrocarbon mixture consisting largely of olefins and containing constituents boiling all the way from 150° to 300° C. (302°–572° F.). The reaction vessel consisted of a malleable iron tube three feet six inches long by four inches in diameter, electrically heated by nichrome wire set in alundum cement, a rheostat being provided for accurate control of the temperature. The tube was filled with a pure iron oxide (of paint grade) prepared from copperas, the tube being nearly filled with the unground material, in lump and powder form. The temperature was measured by means of a thermocouple on the outside of the tube which had previously been calibrated with a thermocouple in the center of the oxide so that the temperatures mentioned are internal.

The oil was vaporized and the vapors carried through the tube and discharged into a condensing system. At the beginning of the operation the temperature reading was 580° C. (1076° F.) for a boiling point of the hydrocarbon introduced of 150° C. (302° F.) and this temperature was gradually increased in proportion to the rising boiling point of the hydrocarbon to an ultimate temperature of 750° C. (1382° F.). The pressure within the system was sufficient only to maintain the

regulated flow of the vapor therethrough. The condensate amounted to upward of ninety per cent of the oil treated. Of the recovered product forty-seven per cent boiled under 180° C. (356° F.). The remaining high-boiling material was refluxed, to be again subjected to oxidation.

The material boiling under 180° C. was fractionated, yielding a series of fractions as follows:

Up to   40° C., about 7 %, largely amylene.
40 "   75° C.,   " 8 %,   "   hexylene.
75 "   95° C.,   20–25 %, containing about 70 % of benzol, the balance olefins
95 "   120° C.,   15–20 %, containing nearly 75 % toluol, the balance olefins.
120 " 130° C,   3 %, containing some octylene.
130 " 150° C.,   10–15 %, containing xylols, olefins and some pinene.
150 " 180° C.,   25–30 %, of which approximately 18 % was limonene, the
                           balance largely olefins and aromatic hydrocarbons.

Practically no paraffins were discoverable in the reaction products, which are therefore very readily purified in order to recover their values   For the purpose
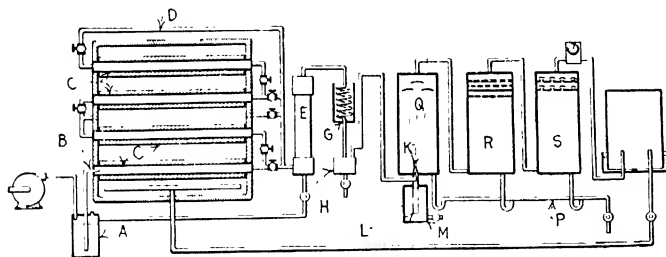
Fig. 176. — Apparatus proposed by Ramage.

for example of recovering benzol and toluol, Ramage proposes merely to remove the olefins by the usual treatment with sulphuric acid, leaving the aromatic compounds in condition for rectification.

Figure 176 shows a tank A for containing the starting material from which it is delivered to a nozzle B by pressure upon the liquid in the tank.   The hydrocarbon is thus injected into a series of connected tubes C containing the reducible oxide, these tubes being mounted in a furnace.   From the tubes a pipe D leads to a reflux condenser E, maintained at a suitable temperature   From this condenser the residual high-boiling point material returns to tank A for retreatment

The uncondensed vapors and gases pass to a second condenser, G, kept at a lower temperature, the condensate being collected in tank H.   The residual gases are then subjected to a scrubbing operation, passing to the nozzle of an injector K supplied with wash oil (which may be some heavier paraffin oil or kerosene, boiling point 180° to 200° C. (356°–392° F.)), through the pipe L from the tank M. This wash oil is sprayed into a chamber provided with baffles, the separated liquid passing through a trapped pipe to the collecting main P   The vapors and gases pass from chamber Q to a tower R, provided with a series of perforated plates, the separated liquid passing to the main P.   The gases from tower R pass to a "bell" tower S, from which the separated liquids pass to main P.   The gases, principally hydrogen, pass to a gas holder.   The wash oils and condensates re-

covered from main P may be reused, after fractioning off the light products, and are returned to tank M.[1]

Mann and Chappell[2] dehydrogenate distillates of petroleum in which hydrocarbons of the naphthene and hydroaromatic, often called carbocylic, series occur to a considerable extent. The object of the process is the production of benzol, toluol, the xylols and other aro-
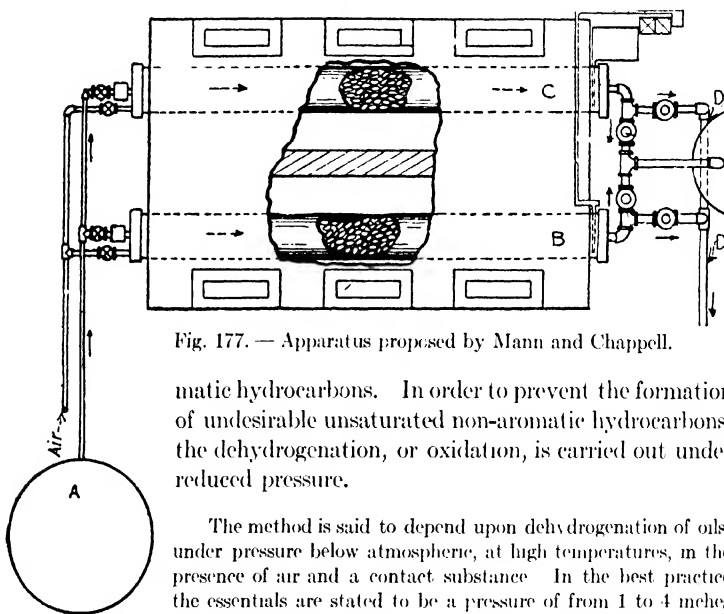
Fig. 177. — Apparatus proposed by Mann and Chappell.

matic hydrocarbons. In order to prevent the formation of undesirable unsaturated non-aromatic hydrocarbons, the dehydrogenation, or oxidation, is carried out under reduced pressure.

The method is said to depend upon dehydrogenation of oils, under pressure below atmospheric, at high temperatures, in the presence of air and a contact substance In the best practice the essentials are stated to be a pressure of from 1 to 4 inches of mercury below atmospheric pressure, that is, 731 6 to 658 4 millimeters of mercury absolute pressure; a temperature ranging from 600 to 750 degrees centigrade (1112°–1382° F); a volume of air from 500 to 800 cubic feet for each 15 or 20 gallons of oil introduced; and a contact substance composed of the lower oxide of a metal. The lower oxide of nickel is recommended. The catalyzer is prepared by impregnating porous material, such as fire-brick, pumice-stone, etc., with the soluble salts of nickel or iron or copper or with mixtures of these soluble salts. The nitrates of these metals are used for the impregnation.

After the impregnation, the contact mass is heated to a temperature ranging from 500° to 600° C. (932°–1112° F.), in the presence of a reducing agent, such as the vapors of petroleum oils.

These investigators state that some of the undesirable oils formed under atmospheric or above atmospheric pressure have boiling points similar to benzol and toluol, and can be nitrated, but explode when heated to the boiling point of nitrobenzol. A reduced atmospheric pressure is used to prevent the formation

[1] See also A. S. Ramage, Canadian Patent 179,252, Sept. 11, 1917.
[2] U. S. Patent 1,214,204, Jan. 30, 1917.

of these undesirable compounds, which cannot be separated from benzol and toluol by fractional distillation, and which, when nitrated, form dangerous explosives.

In Fig. 177, A is the oil supply, B and C a pair of retorts worked alternately, and D the connections leading to the condensers, compressors, and gasometers.

The retorts being brought to the proper temperature, oil is injected into one of them, say B, together with the proper amount of air. Forty-five to 20 per cent of permanent gas and 40 to 75 per cent of aromatic hydrocarbons are formed. The flow of oil is stopped when the catalyst becomes coated with carbon. Retort B is then cut out and C brought into operation. A regulated amount of air is then passed through B in amount sufficient only to burn the carbon deposit to carbon monoxide and hence keep the catalyst in a reduced condition. The carbon monoxide is collected, for fuel purposes, in a gasometer. The hydrocarbon gases and vapors are passed through a series of receivers and condensers, the condensable constituents there being condensed (under slight subatmospheric pressure). The noncondensed material passes through a compressor and is collected in a gasometer.[1]

J. Hausman and **S. Pilot**,[2] by oxidizing crude Boryslav petroleum at a high temperature obtain 23 per cent of distillate boiling up to 150° C. (302° F.) of which about two-thirds is aromatic.

The apparatus used was an iron tube one meter long, 3 inch diameter packed with iron oxide. Crude oil was dropped into this tube, heated to redness and vapors carried through with a current of air.

Internal combustion involving the use of refractory surfaces in the cracking chamber has been recommended by **Ellis**.[3] A vertical cylindrical cracking chamber is filled with fragments of refractory material and at the top heavy oil is introduced in an atomized state. Below this and within the mass of refractory material air in a preheated condition is admitted. Only a small amount of air in proportion to the oil employed is used, as the purpose of the operation is to secure cracking of the oil by burning only a small part of the oil actually introduced into the cracking zone. The path of the burning oil and products of combustion is downward, these being removed at the bottom of the chamber and conducted into a number of condensers from which a series of condensates is obtained, the products of combustion and uncondensed material being discharged from the last condenser. The oil and air may be heated before entering the cracking chamber; the oil by a jacket surrounding the

[1] See also Chem. Abs. 1918, 993; U. S. Patent 1,257,906, Feb. 26, 1918, and Chem. Abs. 1918, 423; U. S. Patent 1,249,444, Dec 11, 1917.

[2] German Patent 227,178, April 1, 1909.

[3] British Patent 25,631, 1912; U. S. Patent 1,295,825, Feb. 25, 1919.

cracking chamber and the air by means of a housing surrounding the first condenser. This is an air condenser through the housing of which air is propelled by a pump directly to the cracking receptacle. The apparatus may be operated under a pressure between 30 and 60 pounds per square inch.

Hirschberg [1] passes oil vapors and mists under pressure in contact with a bulky form of chromium oxide (Cr_2O_3) heated to a dull red. The products are subjected to condensing and scrubbing and uncondensed material is compressed. The raw materials treated include bituminous and mineral oils. The contact body or catalyzer is a light bulky form of chromium oxide obtained by calcining or igniting chromium salts which have volatile bases (such as ammonium bichromate or ammonium chromate).

The following are examples:

A. One hundred kilos of kerosene were led under pressure of 55 lbs. to the square inch into a small tube so heated as to convert the oil to vapors. The vapors were passed into a larger iron tube filled with chromium oxide, prepared as above described and heated to a dull red heat. After passing the catalyzer, the vapors were led into receivers containing heavy oil, such as solar oil. In these scrubbers 53 per cent of the original weight of the kerosene was collected as a light oil of a boiling point between 30° and 170° C. (86°–338° F.) and having a specific gravity of .750. About 26 per cent of the original weight of kerosene was carried away as gas of which about 40 per cent was light oil vapors, the rest consisting of hydrogen, methane, etc. The remainder of the original kerosene, being still a heavier hydrocarbon, was available for retreatment.

After condensation of the light oil vapors and after distillation of the light oil from the scrubbers the yield of light oil (boiling point 30° to 170° C. (86°–338° F.) and specific gravity .750) converted in one operation was 60 to 70 per cent of the original.

B. Ninety-five grams of creosote oil were vaporized and passed over chromium oxide in the manner noted above for the treatment of kerosene oil. After passing the catalyzer, the vapors were led into a receiver, and then through scrubbers, 76 grams of distillate being collected in the receiver and scrubbers, while about 20 per cent of gas was produced. On distillation of the oil contained in the receiver and scrubbers a yield of 30 grams of a spirit of a boiling point between 35° and 160° C. (95°–320° F.) was obtained. From the receiver a distillate of boiling point about 160° C. (320° F) amounting to 46 grams was collected, and this was suitable for further treatment with the catalyzer. From 49 grams of creosote oil, therefore, 30 grams of a spirit of boiling point between 35° and 160° C. (95°–320° F.), representing a yield of 61 per cent, were obtained. The gas contained 44 per cent of condensable hydrocarbons.

C. One hundred kilograms of kerosene of a specific gravity of 0.825 was vaporized and passed at a pressure of about 15 pounds per square inch over heated chromium oxide as described above. After passing the catalyzer the vapors were led into a condenser and then through scrubbers containing heavy oil. In the condenser and the scrubbers after two runs, a spirit boiling between 30° and 170° C.

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[1] British Patent 4573, Feb. 21, 1914.

(86°–338° F.), and having a specific gravity of 0 735 amounting to 63 per cent by weight of the original material, was collected. A further 18 per cent of the original material of a very light benzine was obtained by condensation from the gas, this light benzine having a specific gravity of 0.650 to 0.660. Thus the total yield of light motor spirit was 81 per cent of the original oil treated.

In Fig. 178 A represents a pressure tank for supplying the oil through the pipe B to the furnace C. D is a small pump for maintaining pressure within the pressure tank. The catalyzer is contained within the retort E and is heated by
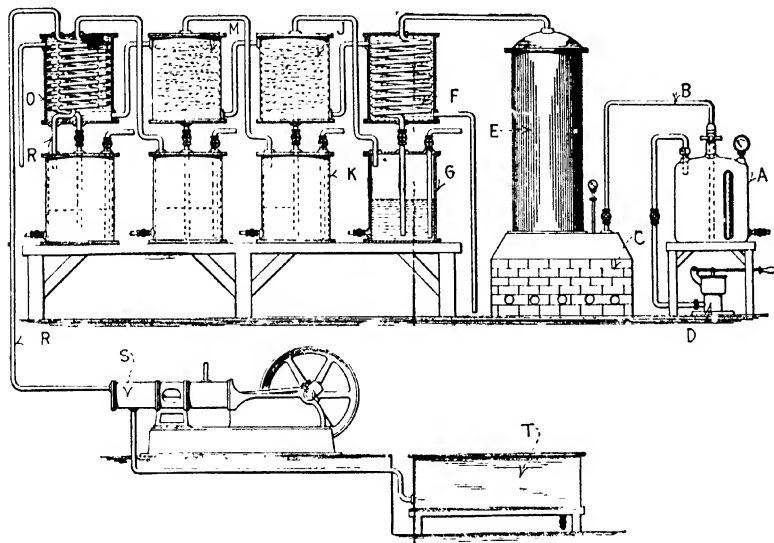
Fig. 178. — Hirschberg's apparatus.

the furnace C. The retort E is connected to a condenser consisting of a coiled pipe F surrounded by a water jacket. The coiled pipe passes from the water container to near the bottom of a second container G arranged below it. The top of this container G is connected to a second condenser J. The end of the pipe J extends to near the bottom of a vessel K. Similarly this vessel K is connected to a third condenser M. The third condenser is connected to a fourth condenser O. In the last condenser O the pipe R leading from the top of the lower vessel P is also arranged partly within the water jacket. This pipe is connected to a compressor S, which is connected to a tank T. The water jackets are connected together and to a cold water supply. Operation is as follows:

Oil to be treated is forced from the apparatus A, by the pressure maintained in it, through the pipe B to the retort E, where it comes in contact with the chromium oxide. After treatment the vapors pass to the condenser F, where the lighter portion of the spirit is condensed and collected in the lower vessel G. The vapors pass from G to a second condenser J and then to the lower vessel K, containing a quantity of heavy oil, which acts as a scrubber. The vapors also pass through two other similar scrubbers and finally are conveyed by the pipe

R to tho compressor *S*. The gases are compressed, and the light constituents condensed and passed to the tank *T*.

J. E. Biggins [1] proposes to burn a part of the oil inside a specially constructed pressure still, in order to furnish heat for the cracking operation. The object is to avoid the external application of heat and in this way obviate some of the difficulties inherent in the usual cracking processes in stills or retorts under pressure. The injection of air at points along the still body causes the combustion which maintains the necessary range of cracking temperatures. The construction of the still body apparently permits using very high pressures.

The cracking temperatures are high enough to permit free development of heat by oxidation or combustion. Stated in one way, instead of keeping up the tem-
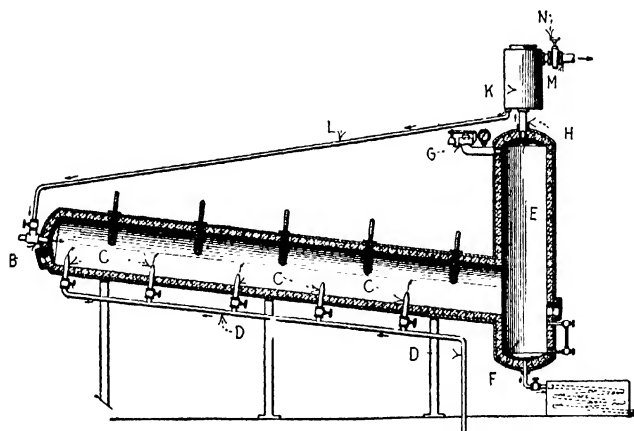
Fig. 179. — Biggins' internal combustion apparatus.

perature within the still by burning oil outside, a little of the oil is burned inside with the net result, it is claimed, of an economy in oil. In so doing, the walls of the still, instead of being of heat-permeable metal, may be brick lined and insulated against loss of heat. The introduction of air, and consequent development of heat, may be at one point or several; but in practice introduction at a number of points in the channel through which the oil and oil vapors flow is desirable to keep a uniform temperature throughout.

The oil or oil vapors unite with the oxygen of the air to form products of combustion (H_2O, CO and CO_2) which pass forward with the residual nitrogen. The presence of the stream of gases going through modifies the operation somewhat. In part, the action is analogous to the action of steam in facilitating the distillation or vaporization of high boiling oils. For this reason, it is necessary to include in the system an air cooled condenser capable of condensing and collecting such high boiling oils as may go beyond the cracking zone and of conducting the

[1] J. S. C. I. 1918, 618A; U. S. Patent 1,274,976, Aug. 6, 1918.

collected high boiling oils back to the cracking zone. With the air cooled condenser between the cracking zone and the water cooled condenser and with a return of the condensate caused by air cooling, the product obtained is asserted to be motor fuel of the nature of gasoline.

Figure 179 shows an inclined still. It is lined with brick and has an outer steel casing which may be further heat insulated. At the upper end is an oil inlet B. If the apparatus is to run under pressure, this oil is introduced under pump pressure Passing through the upper wall of the cracking still are a number of thermometers Passing through the lower wall of the still are a number of air injecting nozzles C, rising somewhat above the lower wall. These are valved and connected to airline D, leading to a source of air under pressure. At the lower end the cracking still communicates with a brick lined vertical tower E, which is a collecting drum and to some extent an air cooled condenser. Generally the temperature in this tower is such as to permit only deposition of tar and carbon. The tower is prolonged downward to form a well or sump F in which the level of accumulated liquid can be seen by a gage glass. At its base is a draw-off connected to a cooling coil. The tower is provided with a safety valve G At the top the tower connects through conduit H with an air cooled condenser, or run back K. From this run back, conduit L is provided for returning condensed high boiling oil It connects with the oil inlet The air cooled condenser has vapor outlet M connecting with the usual water cooled condensers (not shown). There may be a valve in this vapor conduit as indicated at N or there may be a valve beyond the condensers.

Oil is introduced at B. This may be kerosene, solar oil, gas oil, crude oil, or a residuum of distillation. It is said that all kinds of oil may be handled, even those oils which are so rich in carbon as to give a copious separation of coke by ordinary distillation methods. Accumulation of coke does not cause trouble, since there is no heating through the walls If coke accumulates the supply of oil is shut off and coke simply burnt out by continuing the introduction of air. Heavy viscous oils holding considerable water may be handled.

Biggins claims that any desired pressure may be maintained within the apparatus. Since heating through the walls is not necessary and the outer wall may be kept cool enough to take advantage of the strength of cold steel, relatively enormous pressures may be employed. Ordinarily it is not desired to go over a pressure of 100 to 200 pounds. The oil going in at B is vaporized, wholly or in part, by the heat within the cracking chamber; and since it enters suddenly into a zone of high heat, the vaporization takes place in a disruptive way, atomizing any oil not vaporized. Whether vaporized or atomized or remaining more or less in a liquid condition, the oil passes downward, flowing along the lower wall. As it goes, a certain amount of combustion of oil vapors and gases takes place at each of the air inlets, keeping up the temperature. Residual gases, vapors, and oil flow downward into tower E. Here the temperature is still high and any suspended tar and carbon settle out and fall into sump F. The mixture of uncondensed vapors and gases goes forward. High boiling oil is condensed in K, collected and returned to the still. Uncondensed vapors and gases pass forward to the water cooled condenser. The character of these vapors of course depends upon the amount of cooling given in the aerial condenser K. If it is kept at such a temperature that the vapors going through are not above 300° to 350° F. (148°–176° C.), the product recovered from the final condensers will be commercial gasoline, since the kerosene fraction will be collected and returned to the cracking zone. If the vapor temperature is 400° F. (204° C.) or thereabout, the final condenser

will collect a mixture of gasoline and kerosene which may be subsequently separated by ordinary distillation methods.

California oils and other asphaltic oils are distilled to advantage with the aid of air, according to **J. A. Dubbs.**[1] This aids in securing an increased yield of light oils and converts the residue into air-blown asphalt. In Fig. 180 the still A having a pipe, B, leading from a source of air under pressure, is so arranged in coils in the still that the air passing through B will be heated approximately to the temperature of the contained oil before reaching the perforated discharge portion D.

The oil to be treated is charged into the still, which is then heated to the temperature usual in distilling oils. As a spontaneously ex-
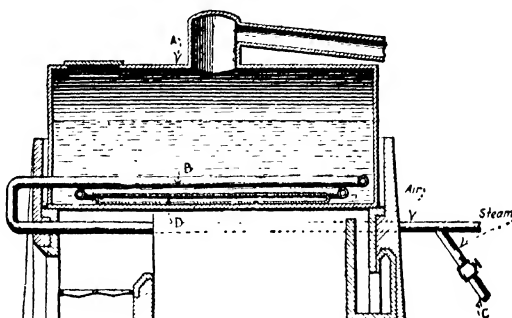
Fig. 180. — Method of blowing oil with air and steam according
to J. A. Dubbs.

plosive compound is formed by a mixture of air and the gases from the oils when the latter form between nine per cent and twenty per cent of the total volume, care is taken when using external heat to heat the oil sufficiently to cause a considerable evolution of gas before the air is admitted. The safe point is evidenced by condensed gases escaping from the condenser. Air is then forced through the pipe B into and through the oil, agitating the oil so as to facilitate the disengagement of the evolved gases. In addition to this agitating function the air, which has been previously heated and dried, will take up considerable quantities of vapor and act as a mechanical conveyor, carrying these vapors into the condensing coil.

By the use of air an increase of distillates is claimed to be obtained from the oil and the character of these distillates is said to be improved. While the cause of this increase in production of light oil is not positively stated, it is believed by the investigator that they result from the splitting of the heavier hydrocarbons

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[1] U. S. Patent 646,639, April 3, 1900 and 1,057,227, Mar. 25, 1913.

by the combination of the oxygen of the air with some of the hydrogen of the hydrocarbons. It is characteristic of the use of air in distillation, especially when applied to the treatment of California petroleum, that the residuum after evolution of the desirable distillates is a true asphaltum and can be used as such without further treatment, while the residuums resulting from the ordinary methods of distillation are petroleum tar or pitch. It is generally believed that in the distillation of petroleum the gases evolved in passing through the oil carry with them some of the heavier hydrocarbons in liquid form and that this mechanical transfer of the liquid hydrocarbons is the cause of the low gravity of the distillate. The belief is expressed that the air prevents this mechanical transference of liquid from the still.

In order to prevent the formation of explosive mixtures of air and gas at the end of the vaporizing operation, the vaporization should be so conducted that the volume of oil vapor generated should always exceed twenty per cent of the volume of air and gas at any time in the still. This can be effected by maintaining vaporization by the continued application of a vaporizing heat until the air is cut off. The time at which the air should be cut off is shown by a reduction of distillate escaping from the condenser. In practice the air is gradually reduced as vaporization lessens in order that the beneficial action of the air may be had as long as possible

It has been found in practice that after the application of heat to the still has ceased there will be a condensation of the vapors given off on the cooling walls of the still and that this condensed vapor dropping back into the residuum in the still has an injurious effect. This action can be avoided by forcing steam through the still at the end of the operation. Hence steam is introduced as the air is reduced, the volume of steam being increased as the air is diminished. The steam can be conveniently introduced by connecting a steam supply pipe C to the air supply pipe at a point outside of the still. The amount of air injected is controlled by the quantity of distillate escaping from the condenser. Generally stated, a cubic foot of distillate corresponds to about ten thousand cubic feet of gas. Hence, by determining the quantity of distillate running from the condenser in given time — say one minute — the volume of air to be forced into the still during the same period can be ascertained; for example, if the distillate is escaping from the condenser at the rate of one cubic foot a minute, thereby indicating the generation of ten thousand cubic feet of vapor per minute, the attendant will so regulate the air-injector that about forty thousand cubic feet of air per minute will be forced into the still. After a few trials, the attendant, by watching the stream of distillate running from the condenser, can determine with sufficient accuracy the quantity escaping in a given time and will regulate the air-injector accordingly, the capacity of the injector being known. While it is preferred to use external heat in connection with the air, the latter may be heated sufficiently high to effect the required distillation without applying external heat to the still. In order to carry on the distillation without the aid of external heat, the air, before reaching the interior of the still, is passed through a superheating coil and there heated up to the required temperature and then forced into the still.

As the demand for gasoline continues to increase beyond the supply one of the natural tendencies is to endeavor to decompose heavy residuums so that part of the latter will be converted into naphtha. The great disadvantage of employing heavy residuums is the fact that

excessive quantities of carbon are formed. Among the methods proposed for surmounting this obstacle that proposed by **W. M. Cross** [1] is of interest at the present time. **Cross** feeds heavy residuum into a pipe heated to about 300° C. (572° F.) very slowly, with the result that complete vaporization takes place as fast as oil is introduced. Considerable carbon is produced under these circumstances, and in order to remove the latter Cross injects air into the apparatus regulating the supply of air so that only carbon monoxide is formed. The vapors in the pipe or retort are maintained under pressure by means of a throttle valve situated at the outlet.

J. Rosen [2] blows coal tar with air to convert it into pitch and simultaneously recovers light oils as distillates.

H. E. Montague [3] constructs an internal combustion engine so that the temperature of the carbureted air is raised to the cracking point to break down the heavier hydrocarbons into lighter ones before the mixture enters the engine cylinders.

[1] U. S. Patent 1,326,851, Dec. 30, 1919.
[2] U. S Patent 1,259,674, March 19, 1918.
[3] Chem. Abs. 1917, 2274; U. S. Patent 1,227,551, May 22, 1917.

CHAPTER XXII

CRACKING BY ELECTRICAL METHODS

The application of electrical energy to the problem of decomposing heavy oils to yield naphtha and motor spirit, particularly those methods that involve the silent electric or corona discharge, represents one of the more promising phases of the general endeavor to find methods for effecting chemical reactions which are less wasteful than those depending on the application of heat energy.

It is known, both practically and thermodynamically, that heat cannot quantitively be converted into useful work, whether that work be mechanical, chemical or electrical, whereas at least in the case of the electrolytic cell, the conversion of electrical into chemical energy may be made to approach quantitative proportions.

It is not until very recent years that, so far as is known definitely, there has been much attempt to apply electrical energy directly to the decomposition of petroleum hydrocarbons. Those methods that involve passing hydrocarbons over incandescent filaments or bodies heated by the resistance offered to the passage of the current, are, strictly, not relevant to the subject under consideration, since in these cases it is heat and not electrical energy that is being directly utilized. The use of the silent electric discharge in this connection does appear to utilize electrical energy directly.

The methods based on this phenomenon will be taken up first.

The Use of the Silent Discharge

Davidson and Ford[1] employ a high tension electric current in connection with gases such as illuminating gas, oil gas, or other gas produced by the destructive distillation of coal or petroleum in order to increase the amount of fixed or noncondensable constituents of these gases. This also has the effect of increasing the volume of the treated vapor.

The unit of apparatus used is an elongated electrode axially centered within a pipe or long cylindrical vessel. The gas to be treated, which may be ordinary illuminating gas at any stage of its manufacture — for example, at a stage preceding the washing and scrubbing operations — is led through the reaction chamber and is subjected to the action of a high tension silent electric discharge between the elec-

[1] Chem. Abs. 1917, 2274; U. S. Patent 1,229,042, June 5, 1917.

trode and the wall of the chamber. The general effect of the discharge is to cause a breaking up of such components into constituents of lower molecular weight, which are not condensable under working conditions, and, hence, to increase the proportion of fixed gases, and to increase the volume of gas produced. In actual tests it is stated that the amount of methane (CH_4) in the gas has been increased from about 25 per cent to approximately 40 per cent, while the amounts of olefins were increased from between 7 per cent and 10 per cent up to between 20 per cent and 23 per cent.

In carrying out the process on a commercial scale, the apparatus shown in Fig. 181 which is similar to that used for electrical precipitation of suspended matter from gases, may be used. In this apparatus the gas is conducted through a number of conduits (vertical pipes) A, connected at their lower ends to a supply header and at their upper ends to an outlet header, the discharge electrode B being wires hung axially in the pipes from an insulated support. The pipes A are grounded and the electrodes B are connected to a mechanical rectifier C of the usual rotary type, included in the high tension circuit of a step up transformer D, the rectifier having a ground connection. The rotor of the rectifier is driven in synchronism with the alternating current in usual manner and the stator contacts of the rectifier may be placed so as to interrupt the circuit at any desired phase relation. By this means the circuit may be broken under conditions which may cause more or less surging and the amount of surging may be increased or decreased as desired. The process may also, in some cases, be carried out by applying alternating current from an alternating circuit or from a transformer directly to the gas to be treated, without the use of any current modifying means.

Fig. 181. — Gas-treating apparatus, according to Davidson and Ford.

Cherry [1] subjects a mixture of burning oil or gas oil vapors, mixed with natural gas to the silent discharge of a bipolar oscillating high frequency current. Under certain operating conditions an 84 per cent conversion of burning oil (kerosene) into naphtha with an end point of 400° F. is reported.

The reaction chamber in which the above conversion is stated to

[1] Trans. Am. Electrochem. Soc. 1917 (32), 345–372.

take place (see Figs. 182, 183) consists of vertical steel pipes 34 feet in length connected in series by means of tees to form one continuous pipe.   These tubes are wound with specially insulated copper cable
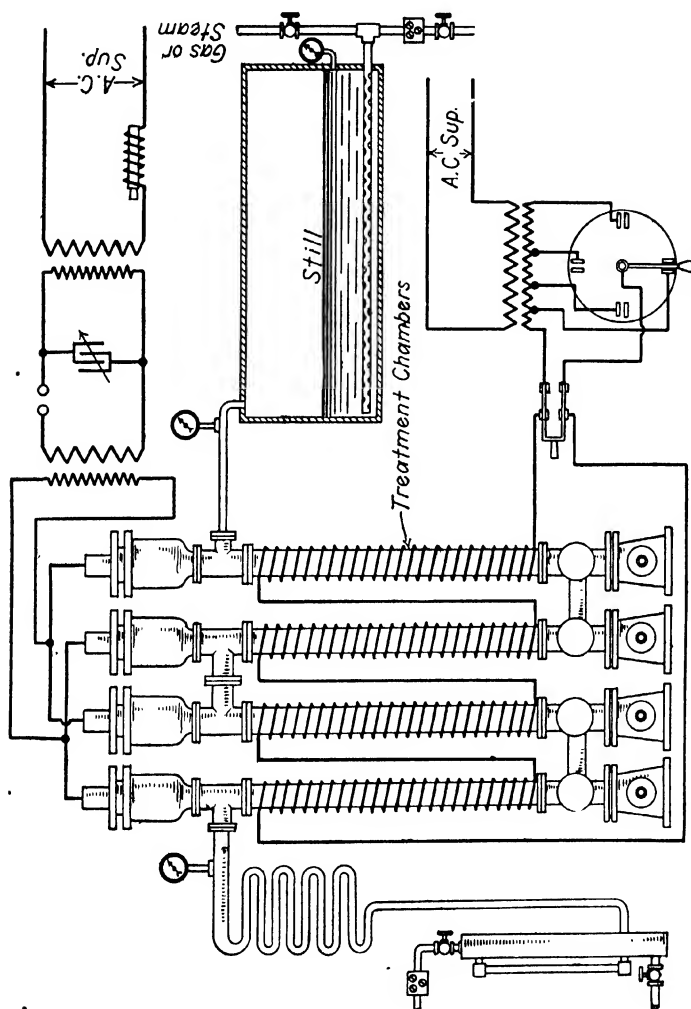
Fig. 182. — Cherry's apparatus for applying the silent discharge of high-frequency electric currents to oil vapors.

through which passes a current for heating the reaction tubes by induction.   The method used consists in passing mixed vapors of natural gas and kerosene or gas oil, at about atmospheric pressure, through the reaction tubes, heating the mixture of vapors and simultaneously

subjecting them to a silent discharge of very high tension and very
high frequency. To accomplish this, a discharge electrode is suspended
in each tube, the walls of the tube acting as the receiving electrode.

The voltage necessary to accomplish the conversion noted above
is stated to be upwards of 100,000 volts [1] with a current of 3–5 am-
peres. The periodicity, also, is required to be of an unusual value
(above the point of audibility, which is given as about 35,000 vibrations
per second). High frequency is said to lead to the production of low
boiling compounds, the higher the frequency the lower the boiling range
of the hydrocarbons produced.

As a possible explanation of this effect of high frequency it is suggested by Cherry
that there may be a quantitative relation between the rates of vibration of the mole-
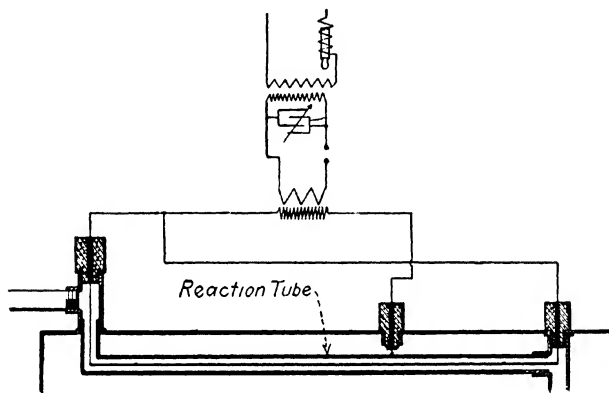
Fig. 183. — Cherry's apparatus for applying the silent discharge of high-frequency
electric currents to oil vapors.

cules of the hydrocarbons formed, on the one hand and on the other of the fre-
quencies of the electrical discharges. The voltage or potential is such that the
maximum amperage passes through the gases without causing arcing. The high
frequency equipment is capable of producing high frequency current from 15,000
to about 250,000 volts, and has a capacity,[2] it is said, of converting into gasoline
about 60,000 gallons of oil in 24 hours.

The 34-foot reaction tubes are connected [3] to a seven barrel still
which distills kerosene at the rate of about one gallon a minute. During
the distillation two cubic feet of natural gas per minute are forced
through the kerosene in the still (the gas at a pressure of 2 pounds per
square inch). Under these conditions, and with the high frequency

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[1] Cherry, Trans. Am. Electrochem. Soc. 1917 (32), 351.
[2] Cherry, *ibid.* p. 358.   [3] Cherry, *ibid.* p. 369.

high tension discharge referred to above, 84 per cent of the kerosene passing through the heated tubes is stated to have been converted into naphtha with an end point of 400° F. One important consideration is the statement that no carbon deposit whatever is encountered so long as the high frequency current is maintained [1] although the temperature of the reacting gases was carried in some instances as high as 480° C. (about 900° F.), also that the product is free from the disagreeable odor of ordinary cracked gasoline, indicating a high " saturated " value.

Discussing the theory of the process, Cherry states.[2] " If we *could* chemically unite, in proper proportion and form, sufficient methane, or hydrogen, to certain of the heavier hydrocarbons, we could produce synthetic gasoline. The amount of gas necessary to do this is surprisingly small, as will be seen from the following table of the paraffin group which shows the percentage, by weight, of carbon and hydrogen in the different steps of the series:

Name	Symbol	Mol. Wt.	Per Cent C (by wt.)	Per Cent H (by wt.)
Methane	CH_4	16	75 00	25 00
Ethane	C_2H_6	30	80.00	20 00
Propane	C_3H_8	44	81 81	18 19
Butane	C_4H_{10}	58	82 76	17 24
Pentane	C_5H_{12}	72	83 33	16 67
Hexane	C_6H_{14}	86	83 72	16 28
Heptane	C_7H_{16}	100	84 00	16 00
Octane	C_8H_{18}	114	84 21	15 79
Nonane	C_9H_{20}	128	84 38	15.62
Decane	$C_{10}H_{22}$	142	84 51	15.49
Undecane	$C_{11}H_{24}$	156	84 62	15 38
Dodecane	$C_{12}H_{26}$	170	84 71	15 29
Tridecane	$C_{13}H_{28}$	184	84 78	15 22
Tetradecane	$C_{14}H_{30}$	198	84 85	15 15
Pentadecane	$C_{15}H_{32}$	212	84 91	15 09
Hexadecane	$C_{16}H_{34}$	226	84.96	15.04
Heptadecane	$C_{17}H_{36}$	240	85 00	15 00
Octodecane	$C_{18}H_{38}$	254	85 01	14.96
Nonodecane	$C_{19}H_{40}$	268	85 07	14.93

" The small increase in percentage of hydrogen necessary to convert some of the heavier fractions of crude oil into the lighter and lower boiling point compounds is thus shown. For example, heptane (C_7H_{16}) contains only 0.51 per cent more hydrogen than decane. On account of the cost of producing hydrogen, natural gas (which is composed mostly of methane, CH_4) was suggested as being

[1] Cherry, Trans. Am. Electrochem. Soc., 1917 (32), 361.
[2] *Ibid.* pp. 346 and 347.

the most desirable, and the following equations illustrate the possibilities of using methane gas (CH₄) to combine with the heavy, high boiling point hydrocarbons, to obtain low boiling point products, if it were possible to obtain such reactions:

Dodecane .... $C_{12}H_{26} + 2(CH_4) = 2(C_7H_{16}) + H_2$
Pentadecane.   ....$C_{15}H_{32} + 3(CH_4) = 3(C_6H_{14}) + H_2$
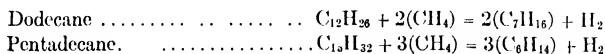
Cherry makes the following statement regarding the possible effect of electrical rupture of hydrocarbon molecules:

" After studying the electromagnetic theory of matter it was conceived, that, if the only difference that existed between carbon and hydrogen (or between two hydrocarbons such as methane (CH₄), and nonane (C₉H₂₀), was the number and organization of infinitesimal units of electro-radiant energy which we are pleased to term electrons, and that if we mechanically mixed the vapors of a hydrocarbon, such as nonane (C₉H₂₀), with methane (CH₄), or natural gas, and impressed upon this mixture electro-radiant energy of the proper periodicity, tone, or keynote, we would be able to break up the 'electronic solar system' of the molecules and cause them to vibrate or 'dance to new music,' and on leaving the zone of electrical action they would assume some natural organization and periodicity depending, to some extent, on the frequency of the energy impressed upon them, and on physical conditions, such as temperature and pressure."

The following data on power consumption and costs is given by Cherry: [1]

One kilowatt of electrical energy used in the reaction tubes will convert 1000 gallons (3785 liters) of distillate in 24 hours, or a 60-K.W plant should convert about 60,000 gallons (227,100 liters) per day; a total of 1440 K.W.-hours are required for the oscillatory current, to treat 60,000 gallons (227,100 liters). It has been found by experiment that 40 K W.-hours of electrical energy are required for heating the reaction tubes while producing 60 gallons (227 liters) per hour, and if the ratio holds true for a 60,000-gallon (227,100-liter) plant, it would take 39,360 K.W.-hours for heating the reaction tubes, while 60,000 gallons (227,100 liters) were being converted; this added to 1440 K W.-hours would make 40,800 K.W.-hours total energy required, which at a cost of 0.6 cent per K.W.-hour would make a total of $244.80, or about 0.4 cent per gallon.

Superheated steam may be used with the gas, or may be used alone. When steam is used, it is decomposed in the reaction tubes, the nascent hydrogen uniting with the hydrocarbons, and the oxygen uniting with carbon, forming carbon monoxide. This is trapped off at the tail of the condenser, and may be burned under the still. Artificial gas may be used where natural gas is not available; in fact, any hydrocarbon or hydrogen-carrying gas may be used. Two or more liquid hydrocarbons of different gravities and boiling points may be mixed and treated, and a compound of different characteristics from any of the original compounds obtained.

While operating, the temperature of the oil in the still is maintained a few degrees below the point that would cause it to distill over and the gas going in at the bottom of the still rises through the oil and acts as a carrier for the oil vapors. In this way, good control of the velocity through the chambers is maintained.

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[1] Cherry, *ibid.* p. 363.

Some of the advantages of this process are stated as follows: Treating chamber equipment comparatively cheap; easily built and installed; small depreciation, as compared with cracking equipment, where precipitation of carbon, together with corrosive action of products of combustion with which they are heated, tends to destroy the plates and tubes. It is observed that the apparatus may be an attachment to the ordinary refining equipment, and utilizes the stills and condensers, agitators and tankage already installed. By converting the distillates between the benzine fraction and that part in which the lubricating oils are found, it is possible, it is said, to increase the output of gasoline 200 per cent.

Cherry [1] proposes a vertical still heated by electricity. A tubular anode suspended in the center of the still causes an upward circulation of oil, due to vapors released and also to the difference in temperature between the oil in the center and that close to the exterior of the still. This strong movement carries the finely divided carbon to the top of the anode and down through it to a settling tank where it settles out. After settling the oil is again carried through the cycle. This process is claimed to do away with carbon trouble.

In **Robertson's** electric discharge process [2] one electrode is a cylindrical vessel or retort, the other is a comparatively large graphite electrode suspended in the retort.

An apparatus proposed by **Robertson** is seen in section in Fig. 184; A and B are retorts surrounded by the hot air jackets J and K. G and P are the graphite electrodes. O is an oil supply. Vaporization takes place

Fig. 184. — Apparatus proposed by Robertson.

(under pressure) in retort A by means of heated air blown through the jacket J. The heated hydrocarbon vapors are said to be subjected to an electric discharge which passes between electrode G and the walls of the retort A and are then retreated in a similar manner in the retort B, through which the vapors pass, on their way to a condenser (not shown). The treated vapors are condensed under pressure and light hydrocarbons separated from heavier ones.

[1] Chem. Abs. 1919, 2591; Oil and Gas J. (1919), (18) No. 10, 68–9.
[2] Chem. Abs. 1917, 3118; U. S. Patent 1,238,339, Aug. 28, 1917.

W. A. Schmidt and **E. R. Wolcott**[1] describe a special method for applying a high tension electric discharge to a single phase or two phase system (gas phase or liquid gas phase). The essential feature is a method whereby the discharge is applied in the form of successive surges of electrical energy, each surge being of short duration and taking place at very high potential. The idea, apparently, is to subject the reacting substances to " ionizing " conditions and to avoid, as much as possible, the decomposition of the products formed by the chemical reactions.

Figure 185 shows an apparatus for treating oil vapors. The casing, or reaction chamber A, is the receiving electrode and in it is suspended the discharge electrode B.
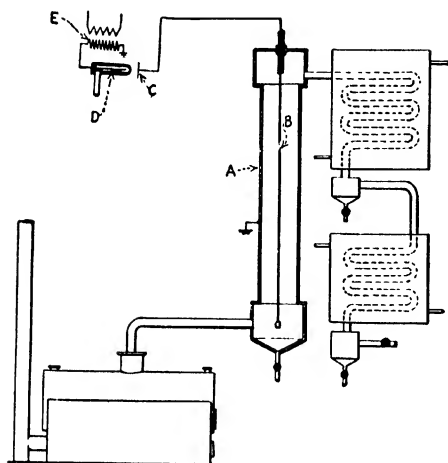
Fig. 185. — High frequency, high potential apparatus for treating oil vapors according to Schmidt and Wolcott.

A is grounded. A rectifier is used to create the surges mentioned. It consists of a plate C and an electrode D. The plate C is connected to the discharge electrode B; and the electrode D is connected to the secondary coil of a transformer E. This secondary coil of the transformer is also grounded, as is the casing A. The electrode D is mounted in an insulated casing, to which compressed air is supplied by a pump. The casing is constructed so that air is blown in the line of discharge between the electrodes D and C of the rectifier, to produce the desired surges.

Oil vapors, generated in the still, pass upwardly through the tube A. They are there subjected to successive surges of a high frequency high potential current. Reaction products pass to the condensers shown at the right. Gases may be mixed with the vapors prior to the treatment of the mixture in the tube A.

In explaining the action of the rectifier in producing a discharge which is more effective in accelerating chemical reactions, it is said that

[1] U. S. Patent 1,307,930, June 24, 1919; see also **Wolcott and Reber**, U. S. Patent 1,188,597, June 27, 1916.

the effect is to produce sudden impulses of high potential and particularly to produce surges or oscillations, in the circuit in which it is connected. Each impulse or surge is of short duration, so that the energy of the surge is applied to the gaseous medium at high potential during an extremely limited time, the high potential resulting in ionization and discharge while it lasts, and the shortness of the time preventing the ionization from accumulating so as to cause break down or disruption. It is said to be characteristic of these surges that the potential differences caused by them are much greater than the applied potential difference in the circuit, produced by the transformer, the surge being due to inductance effect resulting from sudden variation of the resistance of the circuit by breakdown of the gap between the electrodes of the rectifier. It is essential that a considerable amount of the energy of the discharge shall consist of energy due to surging current or of suddenly varying current of steep wave front.

Apparently the conditions under which the apparatus is operated are not such as to produce sustained high frequency oscillations, as no provision is made for an oscillation circuit, including capacity and inductance devices designed to provide for resonance in a local discharge circuit. On the contrary, the impulses produced by the apparatus and which are found to be especially effective in disseminating energy into the gas, are in the nature of isolated impulses, in which practically all of the energy of each impulse is delivered and dissipated in a single surge or wave and is not alternately stored and released as in the case of an oscillating current.

Methods Involving Contact with Bodies heated by Resistance

Adams [1] has devised an interesting process for converting kerosene into gasoline. He maintains a constant level of kerosene in an upright cylindrical vessel. An electric resistance device (see *R*, Fig. 186) is kept submerged beneath the surface of the oil. Cracking is stated to take place practically instantaneously by contacting the

Fig. 186. — Adams' still with electric heater.

liquid oil with the resistance rods which are maintained from cherry red to a white heat. The vapors formed pass up into the vapor space

[1] United States Patent 976,975, Nov. 29, 1910.

S and are constantly removed so that the pressure in the apparatus
does not rise above five to ten pounds per square inch.

The heating elements *R* are closely surrounded by a heat insulating
cylinder *I*. This feature aids in preventing the vaporization, without
cracking, of portions of the oil remote from the heating elements. The
heat insulating cylinder is open at both ends, and since fresh oil enters
through the pipe *E*, the oil must flow upwardly past the electrical
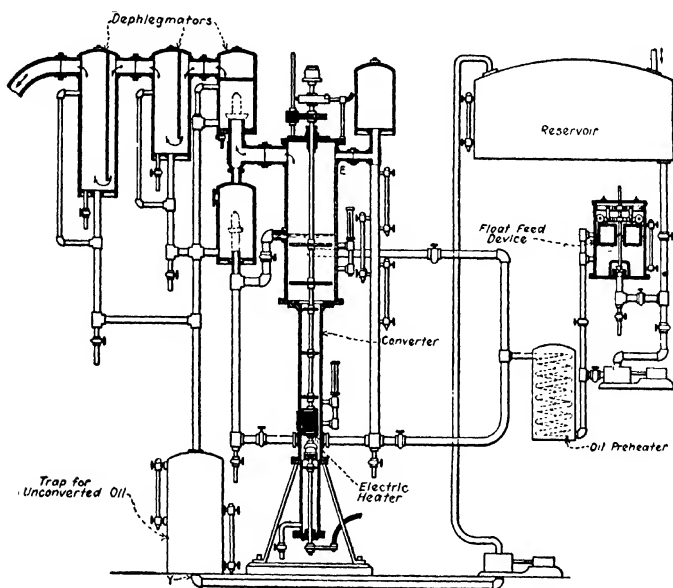
Fig. 187. — Adams' electrically heated still.

resistance. The level of oil is kept constant by regulating the supply
of fresh oil and the removal of vapor from the chamber *S*. Keeping
the heating elements at all times submerged reduces danger from
explosions to a minimum in the vapor space even in the presence of
air or oxygen. The heavier vapors may be returned to the reaction
chamber to be retreated. It is stated that kerosene of 45° Bé. gravity
may be readily changed into a lighter oil of at least 67° Bé. by suc-
cessive treatments.

Figure 187 shows an assembly of another electrical or distilling and
cracking apparatus used by Adams.[1] Treatment takes place either by
a gravity feed, without pressure in the converter, or by forced feed when

[1] U. S. Patent 1,320,354, Oct. 28, 1919.

pressure is used.   A float feed device is employed only with gravity feed.
Oil flows either up or down past the electric heater and the latter
may be stationary or rotatable.   Unconverted vapors are condensed
in a series of dephlegmators and returned to the main reservoir for re-
treatment.   Details of the heater are shown in Fig. 188.

Wassmer [1] uses electrically heated conductors for cracking oil vapors.

Benham [2] forces crude oil through a porous plate, such as unglazed
porcelain.   The oil in its passage through the pores of the septum or
plates is simultaneously subjected to high temperature and an electric
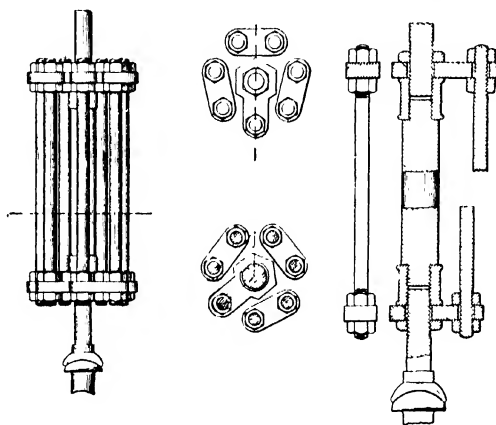
Fig. 188.

potential which is impressed on the moving oil by means of grooved
metallic surfaces insulated from one another and situated on opposite
sides of the plate.

In some of the applications of the process, it is proposed to utilize,
for heating the oil, the exhaust gases from a gas engine cylinder, or from
the tubes of a boiler.   The object is the production of gas and vapor
from liquid fuels.   One of the proposals contemplates operating the
process in conjunction with a gas engine as an integral part of the
appliances of the latter.

Reid [3] destructively distills solid bituminous matter, for example,
coal, asphalt or shale, by means of the heat developed when a heavy
electric current passes through these substances mixed with lime and
charcoal.   The lime is said to react with the carbon left as a residue

[1] British Patent 26,936 (1909).
[2] U. S. Patent 1,040,124, Oct. 1, 1912.
[3] J. S. C. I. 1917, 637A; United States Patent 1,224,788, May 1, 1917.

by the distillation of the bituminous matter and forms calcium carbide. Apparatus is shown in Fig. 189. *C* is the retort or convertor, *E* and *E'* the electrodes and *R* a reservoir for condensed products.

The production of calcium carbide from bituminous shale and lime, and the recovery of the tar or volatile products evolved during the action of the electric current on the composition is described.

A mixture of pulverized bituminous shale and calcium oxide in the proportion of one hundred pounds of bituminous shale to 150 pounds of calcium oxide, are thoroughly mixed and introduced into the retort. It is stated to be advisable to mix with this composition about 5 per
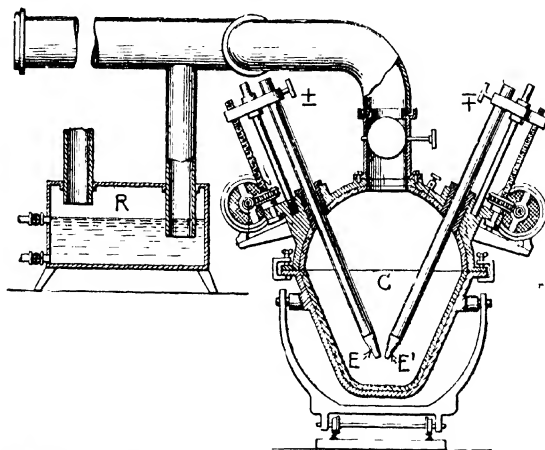
Fig. 189.— Reid's apparatus for distilling coal, bitumens, etc.

cent of granulated charcoal in order to produce a resistance "conductor" and provide for starting the passage of the electric current at a comparatively low voltage, in order to initially heat the mass and render it more or less porous so that the volatile products produced may be readily evolved. When the mixture has been introduced into the apparatus a current of electricity is passed through the mass. As the current passes, the heat generated causes the evolution and distillation of volatile products which condense and accumulate in the reservoir.

When all the volatile products have been distilled off, the residual non-volatile carbonaceous matter associated with the lime is heated to a high degree. and thereby converted into calcium carbide.

Lamplough [1] heats the vapor from a heavy oil to a temperature

[1] Chem. Abs. 1917, 1746; J. S. C. I. 1917, 25; British Patent 16,830, Nov. 30, 1915.

approximately 25° to 50° C. (77°–122° F.) lower than that at which fixed gas is formed or at which cracking will occur. The heated vapor is then passed over electrically heated elements maintained at a dull red heat and the resulting products are led to condensing apparatus.

Figure 190 shows a cross section of an apparatus described by **Hirt**.[1] Oil and steam under pressure are supplied through pipes O and S, respectively, to the reaction chamber K, and the products of the reaction in leaving the chamber expand through valve V and pass through chamber R, thereby preheating the supply of oil and steam. The
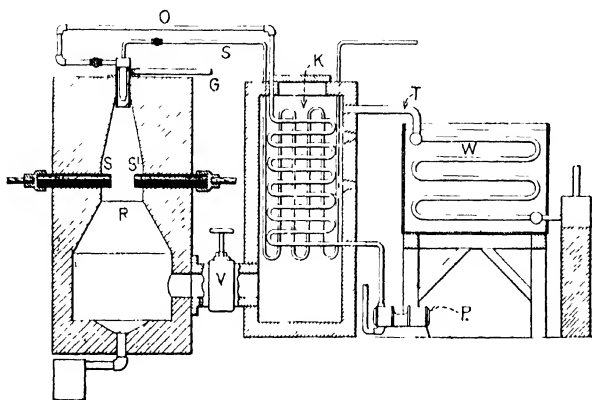
Fig. 190. — Hirt's arc still.

products leave chamber K through pipe T and are further cooled in the coils W.

The reacting substances are subjected in the reaction chamber to the influence of an electric arc. The pressure of the reacting gases can be controlled by the expansion valve V and the temperature of the reaction is regulated by the rate of passage of gases past the electrodes S and S'.

Instead of steam, any other gas which yields or contains hydrogen may be employed, for example, natural gas. Air or oxygen may be used in order to convert free carbon to carbon monoxide. Chlorine may be introduced through pipe G to combine, it is stated, with carbon and form carbon tetrachloride. The lower part of the reaction chamber may be packed with catalytic material to assist in the completion of the reactions.

Maxim, Streatham and **Crosse** [2] convert paraffin oil into a light

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[1] Met. and Chem. Eng. 1916, 98; U. S. Patents 1,250,879, Dec. 18, 1917, and 1,222,402, April 10, 1917.

[2] Chem. Abs. 1919, 72; J. S. C. I. 1918, 617A; British Patent 118,122, Aug. 18, 1916.

volatile spirit and a heavy oil suitable for lubricating purposes by agitating and heating the oil under pressure, and at the same time subjecting it to electrochemical action. The process is carried out in a long steel cylinder, mounted on hollow trunnion shafts midway its length. The interior surfaces are all heavily coated with copper. The cylinder is heated by a gas burner situated beneath, and the gas supply to the burner is regulated by a device placed on one of the hollow trunnion shafts, and actuated by the changes of pressure within the cylinder. The other trunnion shaft carries a pressure gage. The cylinder is first charged to about a quarter of its capacity with paraffin oil, to which is added a small quantity of an electrolyte (e.g., an aqueous solution of common salt or dilute sulphuric acid) together with small pieces of zinc, or V-shaped copper-zinc couples. The air inside the cylinder is pumped out, and, if desired, hydrogen, which may be under high pressure, is admitted. The cylinder is then rotated over the heater until the internal pressure is raised to about 300 to 500 pounds per square inch, which is kept constant for several hours.

This method apparently aims to decompose the heavy oils in the presence of electrolytic hydrogen with a view to obtaining saturated light oils.

In order to effect the hydrogenation of petroleum distillates **J. A. Yunck**[1] heats an emulsion of oil and water in a closed retort or autoclave and subjects the emulsion to electrolysis. The mechanism of the reactions is not definitely elucidated but it is stated that by treating kerosene in this manner large yields of 62° Bé. naphtha are produced.

[1] U. S. Patent 1,345,656, July 6, 1920.

CHAPTER XXIII

THE CONDENSATION OF HYDROCARBONS FROM GASES
NATURAL GAS AND CASING HEAD GASOLINE

Casing head gas is the name given to the hydrocarbon gases which issue with the crude oil from the petroleum wells. In the early days of the petroleum industry the casing head gas was regarded and treated as a waste product, which after being utilized as far as possible for local heating and other purposes was simply burned as the easiest method of disposal, in enormous jets which incidentally provided a tropical climate in the immediate vicinity and illumination of the surrounding country on an unnecessarily lavish scale.

The composition of the gas varies from well to well, and two different qualities of gas are recognized and distinguished by the terms " dry " and " wet." The " dry " casing head gas may consist almost entirely of hydrogen, methane, ethane, propane, and butane, while the " wet " gas may contain these and in addition the pentanes, hexanes, and heptanes, the only normally liquid constituents of crude oil which at ordinary underground temperatures have vapor pressures of such magnitude that they are distilled in quantity from the crude oil. Generally speaking, the amount of gas from an average well, according to **J. G. Annan,**[1] will amount to several thousand cubic feet per 24 hours, and several such wells have to be grouped in order to provide a volume of gas large enough to render the gasoline extraction remunerative. There are two systems of casing head gasoline extraction, termed respectively the " compression " and the " absorption " process. The compression process is most utilized at present, but as the drier gases come to be dealt with the absorption process must also be utilized to a corresponding extent. For gases yielding less than $1\frac{1}{2}$ gallons of gasoline per thousand cubic feet the absorption process is preferred. In the compression process the gas from several wells is piped to a convenient center, where one or more single or double stage compressors are installed which force the gas at a pressure of from 50 to 300 pounds, depending on the nature of the gas, through a series of water cooled metal condenser coils, in which the casing head gasoline

[1] J. S. C. I. 1917, 243.

separates and is collected in suitable tanks also under pressure, while
the incondensable gases are piped away to the point of consumption.
One single unit compressor plant will handle about 500,000 cubic feet
of gas per day.

The absorption process involves passing casing head gas, usually
under pressure, through heavy oil, in which the heavier constituents of
the gas are dissolved and retained by the heavy oil, while the unabsorbed
" permanent " gases pass away to the point of consumption as before.
By a steam distillation of the heavy oil the casing head gasoline is
subsequently recovered and stored in tanks under pressure. The
composition of casing head gasoline is more complicated than might be
imagined from its method of recovery. The physical changes occur-
ring under compression and cooling comprise not only condensation
of vapor and liquefaction of gases but also the solution of the residual
gases in the liquids so produced. Generally speaking, however, the
condensate going to the tanks consists principally of hexane, pentane,
and liquefied butane, but some heptane and liquefied propane are also
present. The yield of casing head gasoline varies with the composition
of the gas, and ranges from eight gallons for a rich gas down to a fraction
of a gallon per thousand cubic feet for a poor gas which would not
repay the cost of gasoline recovery. The average yield, however,
amounts to about $2\frac{1}{2}$ gallons per thousand cubic feet. The total pro-
duction of casing head gasoline, which amounted to only a few thousand
gallons in 1904 and to 30,000,000 gallons in 1913, rose in a few years
to a production of over two hundred million gallons.

At one time much of the casing head gasoline was shipped as such,
but owing to its excessive volatility it was unsuitable as a motor spirit
and somewhat dangerous to transport on account of the pressures
liable to develop under weather conditions, which were by no means
abnormal. Such pressures, amounting sometimes to about 50 pounds
per square inch, were, considering the nature of the material, not
desirable. One method of minimizing this objection was to " weather "
the gasoline by exposing it more or less freely to the atmosphere, so that
the more volatile constituents were dissipated, but the losses thus in-
curred were very excessive and often amounted to 50 per cent in
twenty-four hours' exposure. The method now generally followed,
however, is to mix the casing head gasoline with heavy naphtha in
suitable proportions, causing the objectionable excessive volatility to
be largely reduced, and the mixture can be shipped and marketed as
motor spirit. The specific gravity of casing head gasoline is often as
low as 0.630 and occasionally as low as 0.609 from a second stage com-
pressor. Taking, however, an average figure of 0.645 to 0.648, the

gasoline is mixed with naphtha of about 0.753 to 0.761 specific•gravity in equal proportions, giving a blended gasoline or motor spirit having a specific gravity of about 0.700 to 0.705. Such a spirit would, as far as specific gravity and general appearance are concerned, be indistinguishable from a "straight" or normal refinery product, but the great difference in composition would be disclosed by the results of a fractional distillation. Where the blending has been unskillfully carried out a motor spirit of unsuitable quality might be easily obtained, and the uncertainty regarding this has lead the authorities to investigate the admissibility of fixing a standard of quality to which motor spirit should conform.

J. D. Northrop,[1] reviewing the recovery of gasoline from natural gas, states that of the few industries that may be considered direct offshoots of the natural gas industry the recovery of gasoline from natural gas is the only one that has thus far attained special importance   Though still in process of growth, the natural gas gasoline industry has become a material contributor to the domestic supply of motor fuels from a source whose potentialities in the production of motor fuel are as yet only partly developed.

Although the foundations of this industry were laid in 1903 and 1904 by the experiments of **Fasenmeyer** near Titusville, Pa., of **Tompsett Brothers** near Tidioute, Pa., and of• **Sutton Brothers** at Sistersville, W. Va., and were extended during the period between 1905 and 1908 by the experiments of **Richards** at Mayburg, Pa., of **Hollingshead** at Bradford, Pa., of **McCarty** at Bolivar, N. Y., of **Gray** at Kinzua, Pa., and of others, little headway was made it is said until 1909 and 1910, when the researches of **Peterson** and his associates on the engineering staff of the Bessemer Gas Engine Co., of Grove City, Pa., transformed the industry from an experimental basis to a commercial one.

Its subsequent growth has been phenomenal. In 1911, the first year for which statistics on the subject are available, 176 plants in nine States produced 7,425,839 gallons of raw gasoline from natural gas. In 1917, only six years later, 886 plants in 12 States produced 217,884,104 gallons, a gain in that brief period of 403 per cent in the number of plants and of 2834 per cent in the annual output of raw gasoline.

Prior to 1916 the greater portion of the gasoline recovered from natural gas was obtained from casing head gas, oil well gas, or "wet" natural gas by methods involving compression and condensation. Much of the output came, of course, from plants specially designed and installed to recover the gasoline vapors carried by gas of that type; but a fair proportion, particularly in the Appalachian oil field, was recovered incidentally by the use of simple and relatively inexpensive condensing apparatus connected with vacuum pumps installed to expedite the production of oil, and some was recovered as drips from gas transmission lines. Since 1913, however, a steadily increasing proportion of the annual output of natural gas gasoline has been recovered by the absorption process. The development of this process that followed research work done in 1912 and 1913 by **G. M. Sabolt,** a chemical engineer of the Hope Natural Gas Co., has extended the scope

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[1] Mineral Resources of the Unites States, 1917–Part II, March 17, 1919; U. S. Geological Survey.

of the natural gas gasoline industry to include types of natural gas containing too little gasoline to warrant their successful treatment by compression methods — types that constitute about 50 per cent of the natural gas produced in the country. With the scope of the industry broadened to include practically every type of natural gas found in the United States, its growth since 1913 has been in the direction of increased capacity for production of gasoline rather than in a direction that would tend to determine what other products could be derived from natural gas by variations in the methods employed to recover gasoline. This phase of the industry is now receiving attention, and substantial progress has already been made in the recovery of liquid propane and butane from natural gas in conjunction with the recovery of gasoline. Experiments have demonstrated the feasibility of recovering these two substances at absorption gasoline plants at little additional cost for equipment and operation, and since May 31, 1917, an auxiliary plant of this kind, having a potential capacity of 2000 gallons of liquid propane and 2200 gallons of liquid butane a day, has been in operation in West Virginia.[1]

Liquid propane and liquid butane have fuel values 2.5 to 3 times that of natural gas and have been found suitable for use in cutting and welding metals, in heating and lighting dwellings, and, with the substitution of a gas mixer for the carburetor, as a source of power in internal-combustion engines, both stationary and automotive. Laboratory experiments have shown the possibility of obtaining from the gaseous forms of propane and butane, under certain conditions, as high as 27 and 38 pounds, respectively, of carbon black per thousand cubic feet of gas treated.

These are only first results of scientific research applied in the recovery of gasoline from natural gas. They are sufficient, however, to show that this research, if pursued to its conclusion, will give the resources of natural gas still remaining in the United States an increase in utility and value that may in some measure offset the loss by the notorious prodigality and waste that have heretofore marked our use of this valuable hydrocarbon.

The growth of the natural gas gasoline industry in the United States is shown graphically in the accompanying diagram (Fig. 191).
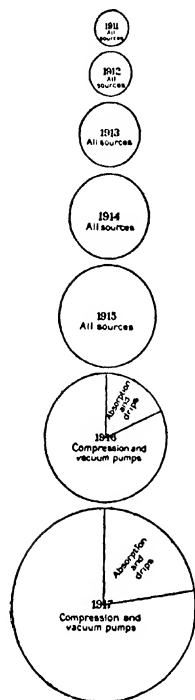
Fig. 191. — Relative quantity of raw natural gas gasoline sold in the United States annually, 1911–1917.

The separation of butane and propane from the " gasoline" hydrocarbons in natural gas is described by **Garner** and **Cooper**[2] The gas

[1] Of the gasoline produced in 1918, 7.5 per cent was from natural gas according to **E. G. Sievers** (Chem. Abs. 1920, 1753); Oil and Gas Journal (1920) (18), No. 45, 68, 70. The average daily production was 774,083 gallons and the total (for 1918) 282,535,550 gallons. Ten of the thirteen states engaged in the industry showed an increase in production. Oklahoma leads in both compression and absorption gasoline.

[2] U. S. Patent 1,307,353, June 24, 1919.

is first subjected to pressure and then goes through absorbers. The enriched absorption oil is then distilled in steam stills under a pressure approximately that used in the absorbers and at a temperature of about 95° to 110° F. (35°–43° C.) The purpose of this pressure distillation at low temperature is to effect a partial separation of propane and butane from the gasoline hydrocarbons. The latter remain, in large part, in the absorption oil. Some propane and butane are also left in the oil, that is, the pressure distillation is not carried to the point where pentane, hexane, heptane and octane begin to come over. The wash oil containing gasoline hydrocarbons is then distilled with steam. Gases which do not condense in the condenser are united with those distilled off in the pressure stills, or retorts. In this way a concentrated mixture of propane and butane is obtained. This is then pumped into a long inclined pipe, where at a pressure of about 130 pounds butane commences to liquefy at ordinary temperatures, it is said, and is drawn off at the bottom of the pipe. By increasing the pressure to about 650 pounds propane is condensed.
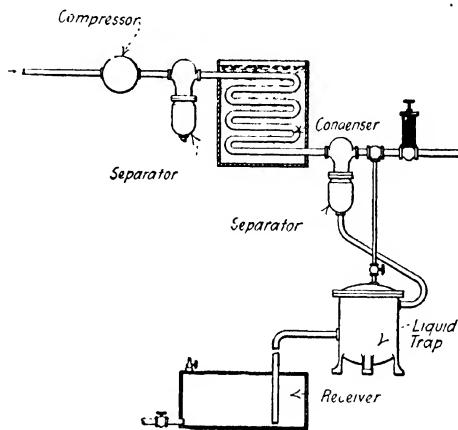
Fig. 192. — Diagram of compression process described by J. L. Gray.

J. L. Gray [1] sums up the basic features of an apparatus for recovering gasoline from natural gas by the compression method as follows (Fig. 192):

(1) A compressor,
(2) A condenser,
(3) A relief valve,
(4) A separator and trap between the relief valve and condenser.

In 1911 **Saybolt** [2] brought out a method for circulating natural gas under pressure (not less than 30 pounds per square inch) in contact with absorbent oil. One of the proposals consists in maintaining a number of series of absorbers, the different series being connected in

[1] U. S. Patent 933,976, Sept. 14, 1909.
[2] U. S. Patent 989,927, April 18, 1911.

parallel, the details of this arrangement depending on the quantity of gas being treated, its naphtha content, degree of absorption desired, etc. (Fig. 193). The absorbers are packed with contact material. In general, the extraction of condensate naphtha takes place on the counter current principle.

The saturated wash oil is then passed through a heat exchanger to a steam still to be "stripped," and subsequently returned to the absorbers. The hot, stripped wash oil, on its way back to the absorbers,
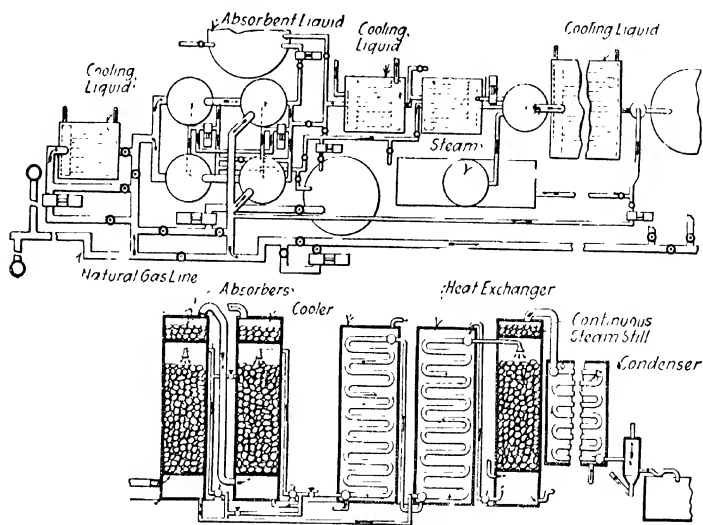
Fig. 193. — Saybolt's process.

is passed through the saturated oil and then through a cooler, before being subjected anew to absorbent action under pressure.

E. Schill [1] compresses casing head gas, natural gas or refinery still gases containing gasoline and other light hydrocarbons such as pentane in the presence of a finely divided "heat absorbing" body which possesses high specific heat, the property of absorbing water, and the property of being a good conductor of heat and which has lubricating qualities. Glycerin, glucose, turkey red oil and trimethylene glycol are given as examples of suitable heat-absorbing agents. If glycerin is used for this purpose it is injected in a finely divided form or mist into a cylinder or cylinders in which the hydrocarbon gases are undergoing compression. It is stated that the heat-absorbing agent, for example glycerin, removes from the gases water, water-soluble impurities

[1] U. S. Patent 1,142,275, June 8, 1915.

such as ammonia and hydrogen sulphide as well as heavier products such as tar. Schill also maintains that heat generated by compression is at least partly absorbed by the heat-absorbing body, and it is stated that the phenomenon of "intramolecular lubrication" prevents the development of as much heat as would take place in the absence of a heat-absorbing and lubricating substance.

The hydrocarbon gases after their compression in the presence of the heat-absorbing agent are subjected to further compression and cooling, in stages, for the extraction of gasoline and pentane respectively.

G. C. Maag[1] has devised an apparatus for carrying out Schill's process, and referring to the latter states that the compression and cooling of the gases is so regulated, together with the use of a heat-absorbing agent, that, as a net result a minimum amount of "wild" product is present in the gasoline obtained. The wasteful process of weathering is therefore claimed to be obviated to a large extent.

. A method described by **A. J. Paris, Jr.,**[2] adapted for the treatment of natural or artificial gases containing aqueous and hydrocarbon vapors, also makes use of a lubricant and heat-absorbing substance. The mixture is first compressed. Oleic acid, lubricating oil, fish oil or castor oil may be used to take up the heat of compression; 1 to 3 gallons of any of these substances is used for each 100 cubic feet of gas compressed to 200 pounds. Cooling and condensation of vapors from the mixture is then effected by expansion, and alcohol or glycerol is used in this step of the process to prevent formation of ice.

Lummus[3] uses a method for recovering solvent vapors from air somewhat similar in principle to the compression method for extracting gasoline from natural gas. The vapors are compressed in two stages, part of the power and cooling effects being derived from the expansion of the cooled denuded gas in an expansion engine.

After going through the low-stage compressor the gas is cooled first by water and secondly by the expanded gas exhausted from the low pressure cylinder of an expanding engine. Condensed liquid is then trapped off and the gas is then passed into the high pressure cylinder of the two-stage compressor. Subsequently it is in turn cooled by water and by the gases exhausted from the high pressure cylinder of the compound expansion engine. Still under high pressure the denuded gas is then washed with an absorbent.

E. H. Sheets[4] heats natural gas under pressure and forces it into

[1] United States Patent 1,142,525, June 8, 1915.
[2] Chem. Abs. 1920, 115; U. S. Patent 1,320,167 and 1,320,168, Oct. 28, 1919.
[3] U. S Patent 1,189,711, July 4, 1916.
[4] J. S. C. I. 1918, 617A; U. S. Patent 1,273,191, July 23, 1918.

a mixing vessel containing heated oil, also under pressure. Vapors from the mixing vessel are condensed under pressure and uncondensed gases are returned to the suction side of the compressor to be again put through the cycle of heating and mixing with oil.

F. C. Devericks[1] recovers a hydrocarbon oil of approximately 85° B. (specific gravity 0.651) from the product obtained by condensing casing head natural gas. A portion of the uncondensed gas is absorbed in low grade oil, thereby raising the gravity of the oil. The resultant oil is mixed with the hydrocarbons of 85° Bé., to produce a liquid of approximately 70° Bé. (specific gravity 0.7000).

S. Davidson[2] describes a process for making gasoline which consists in compressing natural gas and mixing it with a volatile liquid of comparatively low specific gravity; the mixture is then subjected to high compression and condensed. The condensed liquid is passed into a storage tank and the volatilized hydrocarbon vapors are led off to be mixed with further natural gas before compression.

E. L. Kendall[3] extracts gasoline from natural gas by atomizing with it a hydrocarbon of higher boiling point than gasoline, which is at a lower temperature than that of the gas, and then causing the mixed spray containing gasoline and heavier hydrocarbons to pass through a series of screens of different mesh on which the particles of condensable hydrocarbons collect.

Snelling[4] separates natural gas gasoline into heavier and lighter fractions, some of the lighter fractions being suitable for the manufacture of liquefied gases. The method consists in vaporizing the gasoline under a pressure of about 900 pounds per square inch and subjecting the vapors to indirect cooling under this high pressure by means of hot water, warm water, and cold water, respectively. Figure 194 shows the apparatus used. In A the gasoline is vaporized by coils containing superheated steam. The vapors generated pass up into chamber B,
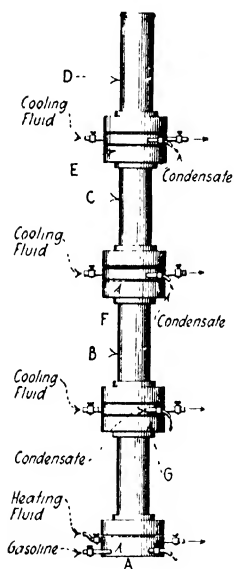
Fig. 194. — Snelling's method of fractionating natural gas condensate.

[1] J. S. C. I. 1918, 294A; U. S. Patent 1,260,970, March 26, 1918.

[2] J. S. C. I. 1917, 1096; U. S. Patent 1,238,644, Aug. 28, 1917.

[3] C. A. 1916, 2297; U. S Patent 1,192,529, July 25, 1916.

[4] J. S. C. I. 1919, 245A; U. S. Patents 1,056,845, March 25, 1913, and 1,259,-679, March 19, 1919.

where coils containing hot water are situated. Condensed material is trapped in the section G and removed from it. Section C contains warm water coils and cold water coils are located in section D.

Refrigeration without pressure is described by **R. O. Wrana.**[1] The gas as it comes from the wells is passed through a series of condensers which contain ammonia expansion coils. The hydrocarbons condense in such a way as to fractionate the liquefiable portion. The advantage of this over the pressure process is said to be its simplicity and every-day dependableness. The color and quality of the gasoline is said to be better. The gas, as it comes from the condensers, is free from moisture. The gasoline ranges from 75° to 85° Bé., and contains 30 per cent pentane, C_5H_{12}, 30 per cent hexane, C_6H_{14}, and 40 per cent higher hydrocarbons. Less than 7 per cent of it is under 50° Bé. It contains no " wild gas " and the loss on standing is less than 2 per cent on 78° Bé. and 5 -7 per cent on 86° Bé. stock.

.   **K. Kharichkov**[2] distills oil to coke in retorts under diminished pressure. Passing through a series of condensers the gas from the retorts is separated from the light and heavy hydrocarbons and is then liquefied by compression and pumped into steel flasks under 100 pounds' pressure. It may be used for household purposes. It contains 46.3 per cent olefins (of which more than half is said to be ethylene), 12 per cent hydrogen, 39 per cent ethane, and the rest methane, butane and pentane. No acetylene or carbon monoxide is present. The calorific value is reported as over 12,000 units per cubic meter.

The following items concerning the manufacture of natural gas gasoline by the compression and refrigeration method are given by **Dykema.**[3]

Use of Combination Compression and Refrigeration Process

Plants of this character are erected to treat casing head gas from oil sands or from sands closely associated with oil, the gas being brought to the surface either between the casing and tubing of an oil well or with the oil in the tubing. The quantity of gas from each well is usually comparatively small and in some installations as many as 500 or 600 wells are connected with one compression plant of not more than the average capacity.

The value of the gas for heating, power, and lighting is not impaired appreciably by removing the gasoline content. If this gas were not

[1] Chem. Abs., 1914, 2245; Petroleum Rev., 29, 423–4.
[2] Chem. Abs , 1914, 3853; Petroleum Rev., 31, 183.
[3] Bureau of Mines Bulletin, 151 (1918).

treated, the gasoline would, at most leases, be burned with the gas used for power purposes and practically be wasted as far as serving any useful purpose is concerned.

First-stage Pressures and Temperatures Used

In plants using two-stage compression, the average pressure developed by the first stage is between 40 and 50 pounds per square inch; the temperature rises to between 200° and 250° F., depending on the temperature of the gas at the compressor intake and the number of compressions developed.

The increase in temperature of the gas from compression is a function of the power used to raise the pressure to the desired point. The power used depends on the number of compressions through which the gas is forced between its initial and final volume. As the amount of power actually expended, and not the initial and the final pressure, determines the rise in temperature, the temperature increase due to a given number of compressions should be the same. If the intake temperatures of the high and the low stage compressor cylinders are equal, the final, or discharge, temperature of both cylinders of a two-stage compressor or of two single-stage machines acting as a high and a low stage unit should be the same, provided they are of equal horsepower and working properly and under uniform conditions.

The compressed gas discharged from the compressor is carried through an oil separator, placed just ahead of the cooling coils, which traps any lubricating oil vaporized in the cylinders or carried mechanically with the gas, the oil being condensed by the time the gas reaches the trap. Cooling to this point is effected by radiation to the atmosphere surrounding the gas discharge pipe and to the jacket water around the compressor cylinder. Some operators employ air cooling extensively in order to save water, the practice being to use a much larger pipe, exposed as far as possible to the atmosphere, for conveying the hot gas from the compressor discharge to the water coils, thereby reducing the speed of flow and so increasing the time of transmission that the temperature of the gas is materially lowered.

Two systems of pipe connections are used between compressor discharges and cooling coils. In one system all low-stage compressors, and likewise all high-stage compressors, discharge the compressed gas into a common pipe or manifold, from which it is distributed by a manifold to the different sets of coils being used to cool the hot gas. The other system is to lead the gas discharged from each cylinder through a separate coil which cools only the gas from that compressor, the gas

treated by each unit being kept separate throughout its entire circuit. The first method has the advantage of permitting one coil to be shut down or cut out for repairs while the compressor is running, the discharge from that machine being cooled in the coils still in use, or conversely, the coil may remain in use while the compressor is idle, and treat gas from other units.   In the second method of connection if any coil or machine is out of commission the entire unit of which it is a part must be stopped, causing more of the plant to be idle.

Throughout the districts making natural gas gasoline the 2-inch pipe in cooling coils is standard.

Direction of Flow of Gas and Condensate

It is universally conceded that the direction of flow of gas and condensate *should be parallel* and not countercurrent. As the liquid will drain toward the lowest point in the coil, the gas must enter at the top in order to flow with the condensate. *It seems that the condensate on long and intimate contact with the gas as above described, is again taken up by the gas as a vapor, even at high pressures, and carried to some point more conducive to precipitation and separation.* Hence counter current flow is not advisable.

That condensate vaporizes in accumulator tanks has also been proved and has given rise to the practice of trapping off the liquid as soon as collected. Because of the facts stated, it appears to be the best and most productive practice to separate the gas and condensate as soon as possible after all the condensable fractions have been precipitated and always to allow the gas and condensate to flow in the same direction. If the above arguments hold true under all conditions, it would seem to be advisable to divide the gas to be cooled into a number of coils or pipes that will retain it only long enough to obtain the maximum cooling effect from the water used, and to separate the gas and condensate as soon as possible.

The proportion of condensate collected in the low-stage accumulator tanks averages 15 to 30 per cent of the total yield and varies between nothing and 40 per cent, depending on the content of condensable fractions in the gas and on the temperature and the pressure used. Some operators permit condensate to accumulate in the tanks until the entering gas is forced to pass through it, or to accumulate for a given time, and then run it into the storage tank through a hand valve. The general practice, however, based on the theory that to separate gas and condensate as soon as possible produces the best results, is to remove the condensate from the accumulator tanks continuously with a small automatic trap that dumps often and with but little agitation keeps the tank practically empty at all times.

High-pressure Treatment

From the low-pressure accumulator tanks the gas passes into the high-pressure cylinder of the compressor, and the cycle is repeated except that the higher pressure causes the lighter hydrocarbons to condense.

A somewhat larger cooling area is used for the high-pressure gas. The area of high-pressure coils per 1000 cubic feet of gas cooled daily is between 0.7 and 0.8 square feet and about 4.5 square feet per horsepower used in compression, while that of the low-pressure coils averaged between 0.6 and 0.7 square feet per 1000 feet of gas and 3.5 square feet per horsepower. If the same amount of power is used by each cylinder of the compressor, there seems to be no reason why one cooling area should be larger than the other, unless the gas is not cooled in the low-stage coils to the temperature later obtained in the high-pressure coils.

Perfect cooling between low and high stage compression implies cooling the gas before it enters the high-pressure cylinder to the same temperature that it had on entering the low-stage unit. Such cooling is necessary if the two stages are to use the same amount of power in compressing equal quantities of gas an equal number of compressions. In compression plants with imperfect cooling between stages the work in the cylinders is allowed to take care of itself in such a way that the number of compressions in the two stages is not exactly equal. In general, to keep the gas at the lowest practicable temperature at all times during treatment is the best practice. From the high-pressure coils and accumulators the gas passes to the field fuel lines or, if expanded gas is used to reduce the temperature still lower, it is led to the high-pressure coils cooled by expanded gas.

Methods of Expansion

At many plants the gas after treatment in high-pressure water-cooled coils and accumulator tanks is further cooled, still at maximum pressure, in heat interchangers or double-pipe condensers by expanded gas. Two methods are used to obtain low temperatures by the expansion of gas, (1) expanding the gas through a small opening or valve to a lower pressure, thus producing the absorption of heat, and (2) expanding the gas adiabatically in the power cylinders of a steam power unit, such as a compressor, pump, or drilling engine.

Expansion through an Orifice or Valve

In the first method the high-pressure gas carrying some gasoline not removed by previous treatment is passed through either the inside or outside pipe of a double-pipe heat interchanger, and the dry gas is expanded through a small opening, such as a ½-inch valve, between the pipes, thus cooling the high-pressure gas and causing further condensation of gasoline. The high-pressure gas and the condensate are led to an accumulator tank, where the condensate is collected and removed. From the accumulator tank the gas passes through the expansion valve of the heat exchanger and the pressure is lowered to 10 or 15 pounds, or the pressure desired or necessary to carry the gas through the field lines. The refrigerating effect obtained by this method is surprisingly small, and although many coils using this principle for cooling have been installed, few of them lower the temperature of the high-pressure gas enough to be of material benefit. In certain standard installations one coil of this type is installed with each high-pressure unit, the inside pipe of the coil having a diameter of 3 or 4 inches, and the outside 6

or 8 inches. The length is usually approximately 80 feet, and either the straight-line or return-bend type is used. After leaving this coil the gas is returned to the field for use on the lease, or sold to commercial gas companies.

The temperatures produced by heat exchange on high-pressure gas vary in practice from $-17°$ to $+65°$ F., or between 75° below and 20° F. below atmospheric temperature. The best temperature to use in a given plant depends, as does the ultimate high pressure used, on the characteristics of the gas and the product desired, also on the efficiency of extraction and temperature previously obtained in the water-cooled coils. As the condensation of vapors depends on both temperature and pressure, in accordance with the physical laws of gases, at a given pressure there is some critical temperature below which it is useless to cool the gas.

At all plants where expansion units are used, the development of power by the expansion of the gas has been a secondary consideration. In a number of plants power is developed only to give resistance to the expanding gas, as in a plant using a pump under a back pressure of 150 pounds, and in another plant compressing air to 40-pound pressure. The amount of power developed in an expansion engine as compared with the amount used in compression is very low, probably not more than 5 or 10 per cent in average plants. This condition is to be expected because of the energy loss through dissipation of heat, the consumption of power in operating the piston and valve in the expansion cylinder, and the reduction in pressure through losses of gas and vapor by condensation and leakage during transmission through pipes and cooling systems.

In expanding compressed gas for power purposes only, and not for refrigeration, preheating the gases by either the hot compressed gas or the engine exhaust would be necessary in order to make the installation a commercial success. Using a relatively small quantity of gas at a low temperature (60° F.) would hardly pay in power delivered, as compared with a gas engine using gas worth 15 cents or less per 1000 cubic feet.

Condensate from Low- and High-pressure Coils [1]

The first condensate produced in treating gas by compression is the small quantity of rather heavy and often discolored naphtha accumulating in the pipe-line drips. After this condensate has been collected and cleaned by filtering or distilling it is mixed with the balance of the plant product, giving the mixture a lower gravity and vapor tension and helping to stabilize the "wild" condensate from other parts of the plant.

The second condensate is that collected in the low-pressure accumulator tanks; its proportion to the whole product varies between nothing and 50 per cent, and in average plant practice between 10 and 30 per cent. The gravity varies around 60° Bé. and the vapor tension

[1] Dykema, *ibid.* p., 57.

between 1 and 3 pounds. Such condensate makes an ideal motor fuel just as it comes from the coils, but is usually mixed before leaving the plant with the other products either in " make tanks " or in storage tanks, having the same tendency as the line drip to improve the product as a whole.

Next in the series of condensates collected is that obtained from the gas under the maximum pressure used in any given plant and at temperatures developed by water cooling.

In average plant practice the condensate precipitated and collected at this point represents the principal bulk of the total recovery, seldom being less than 30 per cent of the total product even in plants using expansion units, and at times reaching 100 per cent, as in all single-stage practice and in some two-stage installations.

The specific gravity of the high-stage condensate is between 65°–100° Bé., averaging in eastern fields approximately 85° Bé., in Oklahoma 78° Bé., and in California 72° Bé.

As formed in the accumulator tank this condensate is " wild," owing to the absence of low-gravity fractions, to the presence of dissolved gas, and to hydrocarbons that are liquids only under high pressure at the temperatures attained in the water-cooled coils. As the pressure is reduced by the automatic traps or in the transfer from accumulators to the " make " or storage tanks, the lighter fractions and dissolved gases immediately start coming off and build up pressure in the tank containing them or escape to the atmosphere. For these reasons the condensate from high-pressure accumulators is usually discharged to tanks containing the heavier fractions precipitated in other coils and is often blended in there, or before it reaches the storage tanks.

The condensate from expansion coils has much the same physical characteristics as the condensate from high-pressure water-cooled coils and is handled and treated in the same way.

It appears that different natural gas from different fields containing the same quantity of condensable vapors seldom contains the same percentages of the various hydrocarbon fractions entering into the composition of gasoline. Thus, in part at least, explains the wide variation in the gravity and amount of product obtained under similar conditions of temperature and pressure in different plants treating gas from different parts of the same field or from different fields.

Blending and Shipping the Condensate,[1]

Reasons for Blending

When the condensate produced by compression is allowed to weather unblended until its vapor tension is reduced to less than 10 pounds

[1] Dykema, *ibid.*

at 100° F. and its temperature rises to atmospheric, losses ranging up to 75 per cent of the total product often result, while if the condensate is mixed (blended) with heavier straight still-run refinery distillates the losses from weathering are reduced, usually to one-half that amount, and often more. This fact has led condensate producers to take advantage of blending to increase the volume of the product actually marketed, thus increasing their profits and also the supply of marketable motor fuels so desirable under present conditions. The development in gasoline motors up to the present time has not reached a stage that would make the heavier still distillates, such as are used for blending, a convenient or economical fuel if used as made, because of the difficulty in starting the motor with such fuel and its tendency to deposit carbon in the cylinders and on the pistons from incomplete combustion, causing " engine trouble."

Condensate produced by compression is also an undesirable fuel for gasoline engines. It is exceedingly volatile, which causes losses in handling, is dangerous because fumes are easily formed, and gives less power as compared with equal volumes of heavier distillates, a larger number of gallons being required to develop the same power. It gives a quick, sharp explosion in a motor cylinder, but seems to lack " push " after the explosion has taken place. In the above qualities it is in no way different from still-run products of similar gravity and similar end points, both products needing additions of less volatile, heavier, and more powerful fractions in order to form the most convenient and economical motor fuel.

The lighter fractions of petroleum distillates, as compared with the heavier products, have a lower calorific value per gallon but a higher calorific value per pound. As all products of petroleum are sold in the United States by volume or liquid measure, the standards for comparison must be made on the heat units per volume and not per weight.

Another important factor in blending is transportation. The Interstate Commerce Commission rules controlling shipments of petroleum products and liquefied natural gas allow transportation of petroleum distillates having vapor tensions of less than 10 pounds per square inch in standard tank cars, and products with vapor tensions of 15 pounds per square inch in specially built insulated tanks. As many plants produce condensate that has a vapor tension of 30 or more pounds as it comes from the accumulator tanks, blending and weathering are both resorted to by most manufacturers in order to bring the product within shipping rules, to increase the quantity, and to improve the quality of the product.

Methods of Blending

Blending condensate with the various distillates used for that purpose, as practiced at present, is done at times in stages, and at many different points in the precipitation, storage, or transportation of the product. The product of plants that ship their condensate without being blended usually goes to refineries or blending stations belonging to purchasers of this type of product, who blend the condensate before sending it to the retail markets. One blending company in West Virginia buys condensate, pumps it to the plant in pipe lines, stores it in closed tanks until needed, then blends it with naphtha in the following manner:

A tank of naphtha is one-half unloaded, usually into an empty tank car, and then condensate is slowly pumped in through a valve in the bottom until the tank is filled. The condensate rises through the naphtha and slightly agitates it, and in this way becomes absorbed and blended with the naphtha. At times the operation is reversed, a tank car being half filled with condensate and the naphtha pumped in from above. No further treatment is used, the car being shipped as soon as filled. The agitation during shipment tends to complete blending if such is necessary.

Blending practice at some refineries and casing head gasoline plants is practically the same as described above except that stationary tanks are used in place of tanks on cars. At other blending plants a pump is used in blending, its suction being connected with two tanks, one of blending stock and the other of condensate. The flow of each is regulated in the pipe line by valves, the discharge of the pump going to a storage tank. From time to time the mixture in the storage tank is tested for gravity, if the blend is too light or too heavy the flow of either naphtha or condensate is adjusted to give the desired mixture.

At some plants methods of blending are more complicated. The procedure used is as follows: A given quantity of California distillate with a gravity of 53° to 55° Bé. is placed in a cone-bottom blending tank, where it is washed with acid solution, caustic solution, and water; after this treatment condensate with a gravity of 72° to 82° Bé. is forced into the tank from the bottom. Air is then blown through the mixture to agitate it and remove the lightest fractions of condensate and dissolved gases. The mixture is tested for specific gravity, after which enough still-run California gasoline with a gravity of 58° Bé. is added to bring the whole to a gravity of 60° Bé. The blended gasoline produced by the above method and ingredients is sweet, water white, and has the following characteristics: 5.9 per cent distills over up to 140° F. (60° C.), the distillate having a gravity of 79.9° Bé.; 70 per cent distills over up to 246° F. (119° C.); and 30 per cent distills over between 246° and 344° F. (119°–173° C.) Distilling this blended product in 5 per cent cuts shows it to be an exceptionally good motor fuel with none of the usual fractions missing.

While holding condensate in storage some blending companies and refineries, as well as compression-plant operators, keep the tanks containing such stock under pressure and often the tanks are insulated or housed and shaded in order to reduce evaporation by the sun and the atmosphere.

Plant Blending Methods

Plants at which blending is entirely or partly completed have developed methods and practices quite different from the usual way

of mixing the two constituents in a blending tank. Many plants still blend the condensate and the naphtha in storage or blending tanks, using the methods previously described above, but a tendency has developed for blending at much earlier stages of the process.

The first step in this development was when certain operators pumped blending naphtha into the tanks known as " make tanks," which receive the condensate from the accumulator tanks, and in which the total make of one day or shift was measured before being transferred to storage. The method as now used is to pump naphtha into the tank at such a rate that the percentage in the mixture would be somewhat below that desired in the final blend, or to place a given quantity of naphtha in the make tank and discharge condensate from the accumulators into the naphtha. In transferring condensate from the accumulator tank to the make tank, the sudden release of pressure causes violent weathering or boiling, owing to the high vapor tension. By adding heavier blending stocks at this point the vapor tension is lowered, with consequent lessening of losses from the light condensate and dissolved gas weathering rapidly and carrying off with them part of the heavier fractions.

The product of this blend is gaged in the make tank, the quantity of naphtha deducted, and the actual plant production calculated. At the end of each day or shift the mixture is transferred to storage tanks and the blend completed or shipped to another point for blending as described above.

Blending in accumulator tanks consists of pumping naphtha slowly and continually into the tanks, connected with the high-pressure coils, at a pressure a few pounds in excess of that at which the gas is being treated. The naphtha is injected into the tank through small ($\frac{1}{2}$-inch) pipes at a point near the top and through fittings which cause a spray, the theory being that the spray will collect fine particles of condensate in falling through the gas and reduce the gravity and the vapor tension of the product before it is released from the high pressure at which it is precipitated and thus reduce losses of condensate.

Operators using this method claim it produces a marked increase in plant production, one in particular claiming a net increase of 10 per cent. The mixture is drained from the accumulator tank as in other practice, either automatically or by hand, as the custom of the plant may be, the quantities being figured as previously described to determine the plant production.

When naphtha is injected into the high-pressure gas while it is in the coils, or before it has reached the coils, and is still hot from compression, the method is called " hot blending."

This method has been adopted at some plants where the gas treated contains large proportions of the exceedingly light fractions and the condensate had shown extreme losses in storage and during weathering and blending by other methods. A Pennsylvania operator producing condensate with a gravity of 92 to 95° Bé.

claims a net gain of 15 per cent in marketed condensate from the use of this method, and one in Oklahoma, approximately 30 per cent.

One eastern plant, which compressed the gas to 300 pounds pressure, injects naphtha through a needle valve placed in the high-pressure water-cooled coil header at the intake (hot) end of the coil. The naphtha is pumped through the valve at a pressure of 400 pounds per square inch, which causes it to spray or atomize in the header and intimately mix with the hot gas as the gas divides into the coil pipes leading out of the header. The first few (10 to 15) feet of this coil are kept dry to permit the hot gas to vaporize as much of the naphtha as possible before the gas and the naphtha are cooled by the water sprayed over the rest of the coil.

What happens to the injected naphtha is not definitely known, but it appears that the naphtha is divided into three parts One part is volatilized by the heat of the high-pressure gas carried with the gas into the water cooled coils, and again condensed, thence it is carried to the accumulator tank with other condensate. A second part of the atomized naphtha is probably carried mechanically into the upper pipes of the coil by the flow of gas, where it settles out, owing to the slower rate of flow, and carries with it other condensable vapors. The third part, which is neither vaporized nor carried mechanically into the upper members of the coil, goes to the bottom of the header and flows with the gas through the bottom pipe and blends with the condensate and naphtha in the discharge header, while still under maximum pressure. The mixture then flows to the accumulator tank and thence is trapped into storage tanks

The quantity of naphtha injected into the header is calculated to be somewhat less than is needed to bring the mixture to the gravity desired, the balance being added, in this plant, to the partly blended stock in the make tank, which is also held under pressure. Another feature of the practice at this plant is that the pressure on the blended stock is reduced slowly to avoid violent boiling or weathering. This is accomplished by holding a pressure of 50 or 60 pounds on the make tank while the output of the plant is being transferred to it during a day or shift. At the end of that period another tank is put into service and the pressure on the tank containing the day's "make" is slowly relieved, while the stock gradually acquires approximately the temperature of the atmosphere. At this point the blend is transferred to storage tanks or placed in tank cars for shipment. For each 100 gallons of condensate produced 77 gallons of naphtha are pumped into the coils, which lowers the gravity of the condensate from 90° to 96° Bé. to between 70° and 76° Bé.; later, in the "make" tank, enough eastern naphtha, with a gravity of 58° to 60° Bé., or California distillate, with a gravity of 48° Bé., is added to form a blend of the desired quality.

Naphtha Used as a Blending Stock.[1]

To form an ideal motor fuel, the distillate or naphtha used in blending should be one that will give the mixture a uniform series of fractions between the temperatures at which distillation begins and finishes, with none of the fractions with boiling points so high as to cause incomplete combustion and carbon deposits in motor cylinders. To blend and weather condensate to correspond with the above conditions is

[1] Dykema, *ibid.*

possible, but such practice, because of the great waste and expense, is followed only in blending special gasolines for engine or speed tests.

Rittman, Dean, and Jacobs [1] have shown clearly the differences in still-run and blended gasolines (see Fig. 195), as they are put upon the market. They state that the blended casing head products have larger percentages distilling below 50° C. but have longer distillation ranges, which tend to make the slope of the temperature-percentage curves for these gasolines flatter than those of straight refinery products. They also state that any gasoline having an unusually large distillation cut below 50° C. and with considerable percentages distilling within the temperature ranges of 150° to 175° C. (302°–365° F.) and 175° to 200° C. (365°–392° F.) and being deficient in constituents boiling at intermediate points of the distillation, may be classed as one of these blended products.

The naphtha or distillates being used for blending are those fractions that distill from crude oil after the cuts marketed as "straight still-run" gasoline have distilled off. The naphthas made from eastern and Mid-Continent crudes range in

Fig 195. — Curves showing volatility ranges of refinery and of casing head gasoline. 1, refinery gasoline; 2, casing head gasoline. The flatter slope of the curve for casing head gasoline shows that the content of both low and high boiling constituents is greater in the blended gasoline. After Rittman.

gravity from 46° to 60° Bé., whereas those made from the asphaltic base California crude oils range between 42° and 52° Bé. The difference in the eastern and western distillates is due to the fact that the crude oils in the different fields differ in character, having paraffin, asphaltic, or mixed bases.

The eastern and the California naphthas used in blending have approximately the same end points, although the gravities differ 7° to 10° Bé ; also the blends formed have different gravities, yet the end points, power developed per gallon, and the completeness of combustion of the mixtures are practically similar. The differences in the specific gravities of the various cuts of similar end points from the different crudes decrease as the cuts become lighter.

Numerous blending plants, however, use distillates with as low gravity and as high end point as the kerosene fractions, and, as far as is known, find no trouble

[1] **Rittman, W. F., Dean, E. W.,** and **Jacobs, W. A.,** Physical and chemical properties of gasoline sold throughout the United States during the calendar year 1915: Tech. Paper 163, Bureau of Mines, 1916, p. 27.

in marketing such blends. In using naphthas for blending it has been found that the heavier naphthas give better results than the lighter ones in lowering the vapor tension of the mixture, for equal quantities put in, the heavy fractions having a tendency to " hold down " the light fractions.

In general it may be stated that blended gasoline usually consists of a mixture of half casing head gasoline and half naphtha or distillate, but the proportions vary, depending upon the gravity and vapor tension of both constituents, blending being carried to a point, in conjunction with weathering, that brings the product within the shipping rules and shows maximum profits to the producers.

Stratification of Blended Gasoline

In many quarters belief has been expressed that in blended gasoline the light condensate fractions separate from the heavier distillate fractions, causing stratification. It is true that owing to change of temperature, in a closed tank, the lighter fractions at times vaporize and condense on the sides of the container and drain down, floating in a thin layer on top of the liquid. This condition may have given rise to the belief regarding stratification, but, as shown, is not due to separation of the two or more blended constituents through differences in their gravities. All fractions of petroleum oils are generally e nsidered as soluble, one in the other, and a blend of two or more fractions such as naphtha and condensate should not separate or stratify. All evidence obtainable indicates that no such stratification actually takes place in blended motor fuels through the difference in specific gravity of the members blended. A test made on a California blended product showed no separation. The blend, which was a small quantity of condensate with a gravity of 105° Bé. and a large quantity of distillate with a gravity of 48° B., was placed in a 10-barrel tank and tested after standing one week without being disturbed. Samples drawn from the top and bottom had specific gravities differing only 0.07° Bé. This blend found a ready market as fuel for motor trucks.

The Absorption Process

Von Groeling (Boult) [1] subjects natural gas to a series of steps which involve in each case a higher pressure and a lower temperature, in order to condense out the heavier hydrocarbons in the presence of an absorbing solvent. The method also makes use of the regenerative principle of reduction in temperature by means of the expansion of a part of the compressed gas.

The absorbent used is heavy naphtha, the object, apparently, being to manufacture light naphtha directly without the necessity of distillation to recover volatile products. The absorbent flows continuously through three absorbers in series. Gas also passes through each of the three. In each case absorption takes place by bubbling the gas up through a column of naphtha. The second absorber contains a cooling coil through which partly denuded gas expands on its way to the last absorber. (See Fig. 195a.)

[1] British Patent 30,229, Dec. 24, 1909.
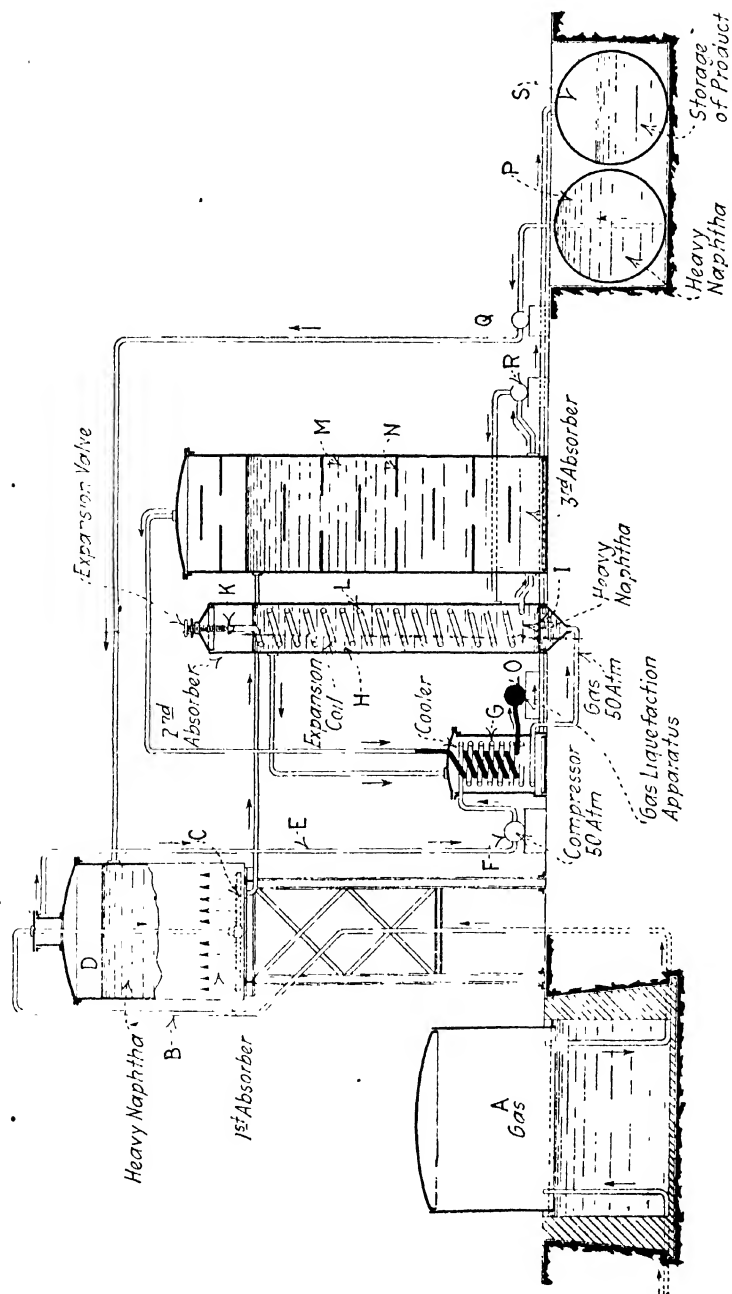
Fig. 195a. — Von Groeling's absorption process.

In Fig. 195a the gas stored in a gas holder *A* is passed through a pipe *B*, which terminates in a distributing device *C*, into the absorber *D*, which is supplied with the absorption liquid. From this first absorber *B* the gas passes to a compressor *F* and then through the cooling installation *G*, from which it is admitted into a second absorption apparatus *H*. The compressed gases enter at the bottom through a fine screen *I*, in the form of small bubbles, slowly rise in the liquid column to the surface, collect there, and pass through a valve *K*, adjustable from the outside, into an expansion coil *L*, which dips into a benzine column.

The cold obtained by the expansion is utilized for cooling the already cooled benzine still further and for withdrawing from it the heat generated during the absorption process. The thorough contact between the liquid and the gas bubbles, the low temperature, and the pressure amounting to about 50 atmospheres result in a thorough absorption of the more easily condensed ingredients of the gas mixture, while the gases not yet absorbed, pass into another absorption apparatus *M*, provided with a series of staggered perforated plates or screens or the like *N*, in order to force the gas to come into contact with the absorption liquid along the longest possible path. From the apparatus *M* the gas passes to the cooling apparatus *G*. The remaining portion of the gas, which cannot be absorbed, is then liquefied in the liquefying installation *O* by the use of high pressure and low temperature. The path followed by the absorption liquid is as follows: From the storing tank *P* the liquid is brought by means of a pump *Q* into the first absorber *D*, from which it flows into the absorber *M*. From the latter the absorption liquid is conveyed by means of a pump *R* into the absorption column *H*, flows through the cooling apparatus *G* and is then drawn into a storing tank *S*. With such an arrangement the gas to be utilized can be treated at varying temperatures and pressures, and the absorption liquid can circulate through the absorbers in such a manner that any desired degree of saturation of the absorption liquid with given portions of the gas can be obtained.

The pressure in the apparatus can be regulated by adjusting the pressure pump, while the temperature can be regulated by adjusting the expansion valve, as the reduction of temperature depends upon the decrease of the pressure.

W. E. Walker [1] distills crude oil by means of the heat contained in compressed natural gas or coke oven gas. He forces the heated gas through cold oil, under pressure. In this way light oils are precipitated from the gas and gasoline is simultaneously distilled out of the crude oil.

Since a reduction of pressure of the gas will be accompanied by a simultaneous reduction in its temperature (assuming that the operation is more or less adiabatic in nature), it follows that, in order to secure the most desirable results, the gas should be substantially up to its initial pressure as it passes through the body of the oil. When it has been enriched by the constituents from the oil, it is cooled to remove those constituents which will precipitate by the reduction in temperature.

If the temperature of the complex body of liquid hydrocarbons is raised to an excessive degree, the process will be accompanied by cracking of certain of the constituents. Consequently, it is desirable to raise the temperature only approximately to 700° F. (371° C.) for the recovery of such lighter hydrocarbons as

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[1] Chem. Abs. 1919, 2276; U. S. Patent 1,307,280, June 17, 1919.

gasoline, naphtha, etc. In separating gasoline, naphtha, etc., from so complex
a mixture as natural gas, it is frequently necessary to raise the pressure to 300
pounds per square inch or even higher. With a strictly adiabatic compression of
the gas to such pressure, the temperature will generally, it is stated, be con-
siderably higher than that necessary or desirable for the subsequent treatment of
the crude oil. Furthermore, it may not be feasible from a practical standpoint
to compress the gas at one stage to such a high pressure as 300 pounds per square
inch, and, therefore, it is the better practice to carry on the compression in two
or more stages. It is stated that the gas may be natural gas, or compressed air;
or, in some cases, hot gases coming off from a retort coke oven.

In Fig 195, A is a tank of sufficiently rigid construction to withstand the
pressure under which the process is carried out. The untreated crude oil is forced
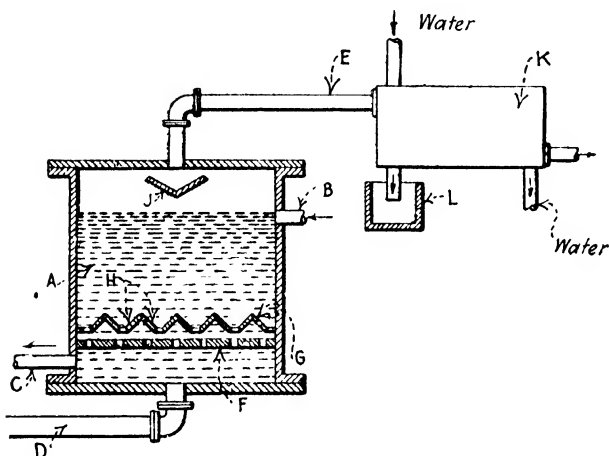
Fig. 196 — Walker's proposal for utilizing the heat in compressed gas.

into the tank through the connection B, and after the process has been completed,
the treated oil is delivered through the pipe or connection C. The gas at high
temperature and under proper pressure is delivered into A through the pipe D, and
·is discharged through the pipe E, after it has passed through the body of the oil.

The process is said to be best practiced by causing the hot gas to bubble
up through the mass of liquid oil For this purpose, the pipe D leads into the
bottom portion of the tank. For a similar reason, a baffle plate F extends across the
lower portion of the tank, and is provided with a number of openings through which
the gas passes in its upward travel so as to distribute it uniformly through the
entire body of oil Another baffle sheet G is placed above the plate F, having a
number of hoods directly over the openings in plate F, and having the intermedi-
ate openings H. In order to prevent the entrance of crude oil into the discharge
pipe E on account of foaming there is a baffle J beneath the opening into the dis-
charge pipe. The delivery pipe E leads to a surface condenser K which is cooled
by a stream of water. By lowering the temperature of the gas in this condenser,
gasoline, naphtha, and other constituents will be condensed and caught in the trap
L. The cooled gas, ordinarily still under pressure, is discharged from this con-
denser through a connection M.

For the purpose of considering what method or methods should be employed in recovering gasoline from natural gas, **R. P. Anderson** [1] uses the following classification. (1) Lean gas, containing less than 0.5 gal. gasoline per M cu. ft. of gas; (2) moderately rich gas, containing from 0.5 to 3 gal. gasoline per M cu. ft. of gas; (3) rich gas, containing more than 3 gal. gasoline per M cu. ft. of gas.

(1) Lean gas is usually compressed for the purpose of transporting it to the point of consumption, but this compression would not ordinarily cause the condensation of gasoline. The absorption method may be employed on gas of this character, provided its gasoline content is sufficient to make the project a financial success. The absorption method has been successfully employed where the gasoline production has amounted to less than 0.1 gal. per M cu. ft. of gas.

(2) The compression of a moderately rich gas for transmission purposes may not result in the condensation of gasoline if the pressure required is low, but gasoline will be condensed if high pressures are necessary. In a gas of this sort the gasoline removal will by no means be complete, even at high pressures, on account of the low initial partial pressures of the gasoline hydrocarbons, and either the refrigeration or the absorption method may be applied on the residual gas, the choice depending upon the local conditions. If the absorption method is to be employed, the pressure need not be raised above the point required for transmission of the gas, while if the refrigeration method is to be employed, the gas should be compressed to 250 to 300 lbs. before expansion, according to the usual procedure.

(3) A rich gas should be compressed primarily for its gasoline content. In this case, on account of the higher initial partial pressure of the gasoline constituents, the efficiency of gasoline extraction will be much higher than in the previous case and treatment of residual gas by refrigeration or absorption method would yield but little gasoline of marketable character. To treat a rich gas by the absorption method at low pressure is an alternative that may possibly have desirable features in exceptional cases.

It will, of course, be understood that no definite figures can be given for the gasoline content at which the direct compression method begins to be applicable, nor for the gasoline content at which the compression method can be made so efficient that no treatment of residue gas is advisable. The figures that have been given for the purpose of setting limits between Classes 1, 2, and 3 are, therefore, only approximate and dependent to a considerable extent upon the nature of the gas to be treated.

[1] J. Ind. Eng. Chem. 1920. (12) 547.

E. S. Merriam[1] proposes to continuously distill gasoline from absorber oil in a specially constructed fire still without the aid of steam.[2] The temperature of the still is automatically controlled by a thermostat and the flow of oil to and from the still is also automatically controlled so as to reduce to a minimum the number of operatives required. Figure 197 shows an absorber in connection with a fire still.
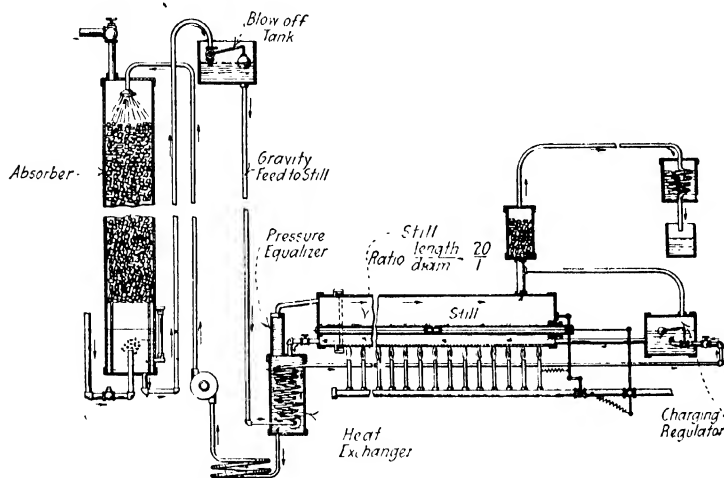
Fig. 197. — Merriam's automatically controlled fire stripping still.

H. Koppers[3] washes out hydrocarbons from natural gas with oil in a bell washer which is placed in a wrought iron jacket into which the gas is introduced so that the pressure within and without the washer is equalized.

Z. Biluchowski and **S. V. Pilat**[4] conduct natural gases of Galicia (possessing specific gravities ranging from 0.820 to 0.892) through cooled benzine or kerosene. These gases then become lighter and 3.6–9.6 per cent of the lighter petroleum vapors are absorbed. The condensed vapors contain 30–56 per cent less aromatic hydrocarbons than the benzine obtained from distillation of the crude oil. The calorific value of the gas, after the removal of these vapors, is reduced from 9136 to 8856 calories.

[1] U. S. Patent 1,304,587, May 27, 1919.
[2] The advantage of continuously distilling a relatively small amount of saturated absorbent, instead of using a larger still, is that a smaller amount of heat is necessary to thoroughly strip the wash oil.
[3] Chem. Abs. 3359; U. S. Patent 1,107,803, Aug. 18, 1914
[4] Chem. Abs. 1915, 1112; Neftjanoie Djelo 1914, 3; through Petroleum 1914 (9), 1305.

C. M. Gay [1] heats crude oil to facilitate atomization without driving off any distillates. It is then atomized with natural gas at about atmospheric pressure and gasoline is separated from the atomized oil and gas by condensation.

J. B. Garner [2] treats hydrocarbon gases containing gasoline with an absorbent oil, first under normal pressure, then under a pressure considerably greater than that of the atmosphere. The pressure is then reduced somewhat, whereby constituents lighter than gasoline which have been absorbed by the solvent are removed. The gasoline is subsequently recovered from the solvent.

J. P. Foucart [3] confines steam at 20 pounds per square inch in a chamber into one end of which natural gas is forced at a higher pressure. Vapor and steam pass out of the other end of the chamber and are led to a condenser.

J. C. Black [4] proposes to secure from, or convert, 50° Bé. oil referred to as " engine distillate " into 60° Bé. gasoline by saturating the engine distillate with natural gas under pressure and distilling. A mixture is produced which is said to have initial and end boiling points identical with those of straight refinery gasoline. It is stated also that under the proper conditions of temperature and pressure, it is possible to obtain gasoline from engine distillate, by passing natural gas through the oil, the gas being forced through the engine distillate, under high pressure and low temperature. After a time, which can be determined by the increase in Baumé gravity, the oil is withdrawn and distilled with steam. The distillate thus obtained can be separated into fractions, one of which will have a gravity of 60° Bé. and boiling points identical with those of natural gasoline obtained from crude oil distillation. A cut can also be made, the gravity of which will be identical with the original stock subjected to the gas treatment. A further cut can be made, the gravity of which will be within the range of that burning oil, or kerosene.

The yield of gasoline will vary considerably with the character of the gas, with temperature, and with the pressure Good results are stated to be obtained where fifty per cent of the engine distillate is converted into gasoline; but it is said that the most economic result is obtained when a conversion is made of twenty-five to thirty per cent, i.e , the maximum yield per thousand cubic feet of gas used is obtained when, upon fractionation, a conversion of twenty-five to thirty per cent is made.

[1] Chem. Abs. 1919, 1593; U. S. Patent 1,179,001, April 11, 1916.

[2] J. S. C. I. 1919, 404A; U. S. Patent 1,299,455, April 1, 1919.

[3] Chem. Abs. 1916, 2522; U. S. Patent 1,195,158, Aug 15, 1916.

[4] J. S. C. I. 1918, 647A; Chem Abs. 1918, 2126; U. S. Patent 1,275,648, Aug. 13, 1918.

By this method a gasoline is produced, it is stated, that is identical with natural gasoline in gravity, initial and final boiling points, and in vapor tension. The gasoline produced is claimed to be different from that produced by mixing casing head gasoline, with a heavy distillate. In this last named case the gravity may be standard, but the boiling points will be low in the initial and high in the final, and the vapor tension will be high in comparison with natural gasoline. A high vapor tension makes the oil dangerous to transport, due to its tendency to create a high pressure when its temperature becomes elevated, and a high final boiling point tends to produce a carbon deposit in the cylinders of gasoline engines

Treating 100 gallons of a low grade distillate (commonly called engine distillate, and having a gravity of 48° Bé. and an initial and
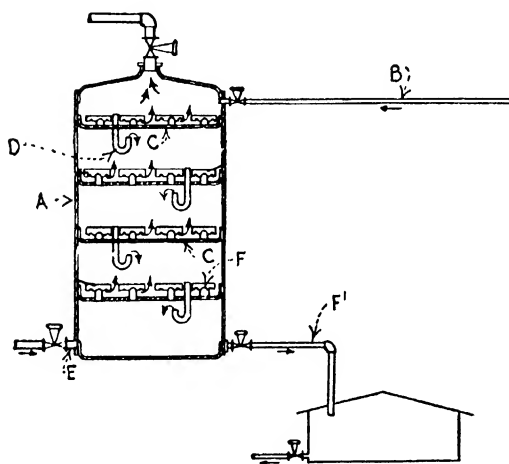
Fig. 198. -- Black's apparatus for saturating engine distillate.

final boiling point of 170° and 436° F., respectively (77°–224° C.)) with 15,000 cubic feet of natural gas, after passing through a compressor plant to take out the casing head gasoline, and under a temperature of 70° F. (21° C.) and a gage pressure of 160 pounds, will cause the absorption of the gas by the distillate in a period of one hour and forty minutes. From the mixture thus formed, upon subsequent steam distillation there is derived a fraction of gasoline amounting to 29.3 per cent of the original volume of distillate, this gasoline having a gravity of 59.5 Bé., and an initial and final boiling point of 94° and 331° F., respectively (34°–166° C.). This is well within the range of the boiling points of natural gasoline, obtained from crude oil distillation.

There is also obtained a cut of engine distillate, the gravity of which is 48° Bé. and the initial boiling point 216° F. (102° C.) and the final boiling point 390° F. (199° C.). The yield of such engine distillate is 60.7 per cent of the original volume of distillate. This engine distillate is well within the range of that obtained from crude oil distillation. The 10 per cent residue left in the still has a gravity of 42° Bé. which is within the range of burning oil or kerosene.

Figure 198 shows a form of treating chamber (A). Oil enters at the top through a line B and flows down over a series of trays C, provided with overflows, D. Gas enters at E and flows upward in a direction opposite to the flow of oil through distributors F. The oil entering at B is under a pressure sufficient to overcome the gas pressure of about 160 pounds. From time to time treated oil is drawn off through F'.

J. B. Weir [1] extracts gasoline from natural gas by compression and cooling, and the partially denuded gas is passed through an absorbent hydrocarbon liquid. The derived products are blended and after a portion of the more volatile constituents has been driven off, the product is ready for use as gasoline. The more volatile constituents thus removed are absorbed by a hydrocarbon liquid heavier than gasoline, and this product is used as the absorbent through which is passed the gas remaining after the initial treatment of fresh quantities of natural gas.

P. Todo [2] saturates the hydrocarbons obtained by distillation of petroleum, etc., with artificial or natural gas under high pressure and at a low temperature. Petroleum is said to absorb five times its volume of coal gas at 32° F. (0° C.) and ordinary pressure. Under a pressure of 8 atmospheres and at 0° F. (− 18° C.), it is stated to absorb eight times its volume of Pintsch gas. It absorbs three times its volume of acetylene at 15 atmospheres, and − 32° F. The resulting product is claimed to be " nearly equal " to gasoline as a fuel.

P. H. King and J. A. Stoneham [3] mix acetylene (98 per cent) and water gas (2 per cent) with an equal volume of hydrocarbon vapor and the whole is condensed to form a liquid containing the acetylene and water gas in solution. The hydrocarbon vapor may be obtained from petroleum or coal tar derivatives having a flash point of about 85° to 100° F. (29°–38° C.).

T. Payne [4] claims to make a fuel analogous to gasoline by subjecting hydrocarbon oils derived from petroleum, asphalt, bitumen, resin,

[1] J. S. C. I. 1919, 36A; U. S. Patent 1,282,338, Oct. 22, 1918.
[2] Chem Abs. 1918, 2247; Japanese Patent 32,460, Mar. 29, 1918.
[3] J. S. C. I. 1917, 1230; British Patent 110,520, June 15, 1917.
[4] Chem. Abs. 1919, 185; British Patent 119,066, Sept. 6, 1917.

bituminous shale, etc., to a treatment consisting in lowering the temperature and increasing the pressure of the liquid in successive stages and at each stage introducing a fuel gas, the product being then restored to atmospheric pressure and temperature.   Kerosene is reduced to about 32° F. (0° C.) under 6 atmospheres pressure and about 5 volumes of coal gas forced in; the pressure is then increased to 8 atmospheres and the temperature lowered to about 0° F. (− 18° C.) and about 8 volumes of Pintsch gas introduced; or coal gas, acetylene, and hydrogen are successively introduced into kerosene at temperatures and pressures ranging to − 32° F. (− 36° C.) and 15 atmospheres. The product is kept under a pressure slightly above atmospheric.

Concerning the absorption process, **Dykema** [1] states that any gas containing the hydrocarbons that constitute the components of gasoline can be treated by absorption for the recovery of these hydrocarbons.   Rich casing head gas and still vapor containing as much as 4 gallons of gasoline per 1000 cubic feet are being successfully and efficiently treated.   The process started, however, in the drying plants of companies pumping lean or " dry " gas which yields only a pint or less per 1000 cubic feet and this fact led to the general impression that richer gases were not amenable to the process.

Effect of Temperature. — Gas should always be cooled to as low a temperature as is practicable without an undue expense for an artificial cooling plant.   The primary reason for cooling is that at low temperatures a given quantity of oil will absorb greater quantities of gasoline; moreover gasoline of a low boiling point will not be recovered by oil at temperatures higher than that point.   Thus low temperature not only increases the total production but also permits a higher percentage of saturation of the oil thereby reducing the total oil circulated. Consequently the pumps, still, and other units have to do less work and fuel is saved.   The oil sent to the towers should have a correspondingly low temperature for the same reasons.

Effect of Pressure. — The pressures being used in the absorption process range from atmospheric to 500 pounds per square inch. Although any pressure may be used, the pressure determines the actual volume of the gas, and this volume is a function of the velocity of flow through a tower of a given cross section.   Thus the pressure, it is noted, controls the cross section or diameter of the towers to be used, since if rate of flow is too great, oil is carried over mechanically and the oil and gas are in contact too brief a time to obtain the desired extraction.   Flow velocities over 75 feet per minute in the unbaffled

[1] Bureau of Mines Bulletin 176 (1919), Recent Developments in the Absorption Process of Recovering Gasoline from Natural Gas.

or open part of the tower are too rapid, so that with such velocities the gas will usually carry oil with it from the tower.

The diameter of the towers used ranges from 18 inches to 12 feet and the pressures from a few ounces to 500 pounds, the low pressure towers being the larger. For high pressure (100 pounds and over) the strength of pipe or metal necessarily limits the diameter.

The percentage of gasoline that is absorbed by the oil is, within the limit of total saturation, controlled by the duration and intimacy of the contact between the oil and gas and the temperature of the two. The duration is controlled by the velocity of the gas and by the height of the effective or baffled part of the tower. This fixes the height of the tower as a function of the saturation desired or possible. Thirty-foot towers are yielding saturations as high as 6 per cent, and higher towers are projected.

Many substances have and are being tried for baffling in towers, the object being to obtain material that will leave the greatest open space for the flow of gas and still break the gas into many fine streams that are continually divided and mixed, and in addition will expose a maximum surface of the absorbent to the gasoline vapors. Wood gratings have been used in different plants and while the work done by them is satisfactory, it is stated that they constrict the tower section unduly and prevent the passage of the greatest volume of gas; that is, they cut down the capacity. Stone filling has the same effect but to a greater degree.

Chemical stoneware, blocks or tile are being used successfully, but they also have a large bulk (50 per cent), which is absolutely inactive as far as concerns useful work. Hollow building tile are also used; they give satisfactory results but lessen the openings considerably. Steel cuttings are being tried, and, so far as the experiments have been carried, seem to give better promise than other material. One company is using 15 pounds of steel cuttings per cubic foot of tower, a porosity of 97 per cent. Another operator uses 30 pounds of the cuttings per cubic foot and has a porosity of 94 per cent. In addition to this high percentage of voids, the material offers an exceptionally large surface for exposing the oil to the gas.

After passing out of the towers the gas is taken through a trap, where any oil carried out of the tower with the gas is separated and run back to the weathering tanks.

Absorption Process. Oil Circuit [1]

Cooling Coils. — Oil entering the towers should be as cool as is economically possible. To obtain this temperature the cooling is done

[1] **Dykema,** Bureau of Mines Bulletin, No. 176, 1919.

in towers under water sprays.   An area of 3 square feet of radiating surface per gallon per minute is stated to be abundant, provided the pipe used is 2 inches in diameter and is placed in a well-designed and properly constructed cooling tower.   The quantity of oil circulated per 1000 cubic feet of gas depends upon the gasoline content of the gas, the pressure, the temperature of both the oil and gas, and the vapor tension of the absorbing medium.   Vapor tension is largely determined by temperature.   As an interesting example of this fact, a company is using gasoline as the absorbent, the vapor tension of the gasoline being reduced by the use of an ammonia cooling plant to the point that permits absorption.   In this plant the product from the tower is a marketable motor fuel and, consequently, redistilling is unnecessary.   It is questionable, however, whether equipment for ammonia cooling can be erected and operated at nearly as low a cost as a still, which, in this instance, it replaces.

Plants using pressures of 100 pounds and higher run the saturation as high as 6.5 per cent, and many operators believe, it is stated, that by increasing the height of the towers 50 to 100 per cent this figure may be increased to 10 per cent.   In plants using lower pressures (atmospheric to 30 pounds) the saturation percentage cannot be brought as high, 2 to 4 per cent being good practice under present conditions.   The richness of the gas in gasoline vapor is of little moment as regards saturation percentages.

From the towers the oil is run through automatic traps to a weathering tank.   In this tank, which is held at low pressures (atmospheric to 30 pounds) the dissolved gases are allowed to separate from the oil so that the subsequent units do not have to treat this gas, a consideration of importance in large, high-pressure plants.   The gas would also dilute the vapors from the still, causing a lower percentage of precipitation in the coils.   These gases with the uncondensed vapors from the still are at many plants treated by compression or in a small absorption unit working under low pressure.   After half an hour to 2 hours weathering the oil is either pumped through the heat interchanger or allowed to flow through it under the pressure held on the weathering tank.

Heat Interchangers [1]

Although many types of heat interchangers have been installed, the industry at present appears to have discarded all types except the jacketed line.   Such interchangers are either made of two pipes, one within the other, each containing oil flowing in opposite directions, and

[1] **Dykema,** Bureau of Mines Bulletin, No. 176, (1919).

connected in series; or of a large pipe with a number (five to eight) of smaller (1-inch to $2\frac{1}{2}$-inch) pipes inside of it so arranged as to give a continuous counter flow of oil. On its way to the still the oil is heated as high as 170° F. while the oil from the still is cooled to 130° F. In coils of the type most used a radiating area of 0.25 to 0.35 square feet is allowed for each gallon per hour passing through the unit on its way to the still.

Stills used in the Absorption Process [1]

With the exception of experiments being made in baffling material for towers, no part of absorption plants is now receiving more attention than the still. The older plants all used the type of steam still used in refineries, but this has proved inefficient in absorption practice. Such stills are 8 to 12 feet in diameter and 16 to 30 feet long. They are held one-third to two-thirds full of oil, which is all partly treated and continuously dilutes the freshly saturated entering oil. The last 1 or $1\frac{1}{2}$ per cent of gasoline contained in the oil is difficult to separate and send out as a vapor, and continual dilution keeps the saturation of the oil in the still at the point where the vapors are most resistant; hence the distilling action requires excessive time as well as an undue amount of heat.

The pan type of still seems to overcome at least part of these objections, as the oil flows through in a small stream while being heated by the steam coils and being treated with live steam in the bottom of the still. The entire operation requires only a few minutes and the separation of the gasoline fractions is accomplished more easily and thoroughly. Vacuum stills and also combination fire and steam stills are being tried.

In distilling an absorption oil with open steam coils (which are necessary if the gasoline is to be vaporized at the temperatures used) not only the gasoline vapors, but vapors of the heavier fractions are driven from the absorption oil itself and these with the uncondensed steam leave the still together. It is now the usual practice to pass this mixture of vapors through some apparatus by which their temperature is reduced through a transfer of heat to the oil entering the still. This transfer of heat is obtained either by direct contact between the oil and vapors or with a heat exchanger of the preheater type, in which the oil and vapors are separated by walls of tubing.

The object of this interchange is to precipitate as much as possible of the heavy oil and water vapors without condensing the gasoline vapors and also to recover a part of the heat from these vapors.

[1] **Dykema,** Bureau of Mines Bulletin, No. 176 (1919.)

From an open contact, or stone tower, which seemingly is not very efficient, the vapor mixture has to be cooled further in water-cooled coils held at temperatures between 180° and 190° F. in order to remove completely the heavy absorption oil fraction carried over. This " knock-out " coil has not been used in plants with a preheater type of unit at this point in the circuit. None of the absorption oil should be allowed to pass this point, as it would condense with and discolor the gasoline. A part of the water vapor will pass this point, but when this condenses with the gasoline it is easily separated by the gravity or the overflow method.

After this point, the gases (gas, gasoline, and water vapors) are further cooled in water-cooled coils.

Final Cooling Coils. — The vapors are often cooled in submerged coils of 2-inch, 4-inch, 6-inch, or 8-inch pipe, having an area of from 2 to 4 square feet per gallon of gasoline per hour. This type of coil is rapidly being replaced by spray-cooled coils in towers. Such coils are generally of the continuous return-bend type, made of 2-inch pipe, enough coils being taken out of a header to care for the volume of gas and vapor to be cooled. The total length of pipe or number of coils of given length is computed on a basis of 2 to 3 square feet of radiating area per gallon of gasoline condensed per hour. The reduction in temperature should cool the vapor as much as the absorption oil and gas entering the towers are cooled; that is, as low as is possible with cooling by water sprays. Gasoline and water are condensed to liquids in these coils and are separated together from the gas. Later the gasoline and water are separated by gravity in any one of the simple apparatus for this purpose or the water is drawn from the bottom of a "make" tank.

The gas from these coils carries some condensible gasoline vapors, and is further treated by compression or with a small (8 inches or 10 inches by 20 feet high) absorption tower. Oil for this tower is taken from the high-pressure oil line leading to the larger towers, and the saturated oil from the towers is sent directly to the still. Between 10 and 25 per cent of the total plant production of gasoline is usually recovered by this treatment. Some operators mix the weathering tank gas with the cooling-coil gases before this final treatment, but the value of this practice is stated to be doubtful.

Gasoline made by the absorption process is especially sweet, has a high gravity (70° to 85° Bé.), and as it comes from the still has a low (3 to 6 pounds) vapor tension. Commanding through these properties a premium in the open market, absorption gasoline is a more profitable product than either raw or blended compression condensate. For this

reason and because absorption plants cost less to install per 1000 feet of capacity and are more efficient than any others in use, absorption plants seem likely, it is stated, to supersede compression and refrigeration plants for recovering gasoline from natural gas.

The use of charcoal as a catalytic agent for reactions between gases has been employed successfully in many chemical processes. During the War it was used to good advantage in the manufacture of phosgene gas from carbon monoxide and chlorine, and found extended application as an absorbent for use in gas masks. Recently charcoal has been advanced as an absorbent for extracting gasoline from natural gas. **Burrell** and **Oberfell** [1] describe their process for recovering gasoline from natural gas by means of charcoal. They state that the charcoal process supplies the demand for a method of extracting gasoline from natural gas which is cheaper of installation than the old process, is more economical of operation, easier to operate, works at one hundred per cent efficiency and may be utilized equally well on rich or lean gas and at high or low pressures.

Three absorbers or three pairs of absorbers are used in a charcoal absorption plant.

These are vertical absorbers and, depending upon the capacity of the plant, will vary from 20 to 35 feet in height and 2 to 3 feet in diameter. These absorbers are packed with a specially prepared, activated, granular charcoal of high porosity. They are so connected that natural gas can be passed through each one in turn. The gas is passed through the first absorber to the limit of the absorption capacity of the charcoal for gasoline, and then is automatically switched to the second absorber.

In the meantime, in the first absorber, gasoline is distilled out of the charcoal and is cooled and collected. In other words, each absorber is a combination still and absorber. When the second absorber has received its quota of gasoline, the gas is automatically switched to the third absorber, and the second absorber starts distilling.

The charcoal in the first absorber is then cooled by means of residual gas from the third absorber before again receiving its charge of gasoline, and thus the process automatically and continuously proceeds with but little attention, working at 100 per cent efficiency and with surprisingly low operating cost. The charcoal lasts practically indefinitely, and actually becomes better with use. The charcoal has a large capacity to absorb gasoline vapor, so that the natural gas passes through one absorber a long time before it is switched to another one.

[1] Petroleum Age, July, 1920, p. 79.

CHAPTER XXIV

BENZOL. USE AS MOTOR FUEL AND MANUFACTURE

With the use of benzol, toluol and other aromatic light oils as fuel for automobile engines we are, in a sense, falling back upon coal as the solution of the problem of motor fuel. Yet as coal is now treated, that is to say by the process of coking, for example in by-product coke ovens, only a minute proportion of the coal substance appears as available motor fuel. Motor fuel derived in this way from coal is a by-product of the steel industry, the main product being coke. The amount of light oil produced at the present time does not satisfy much more than two per cent of the demand for gasoline. Obviously if we are to look to coal as the main factor in the solution of the problem, methods of treatment other than the well-known coking process will have to be employed.

One step in this direction consists in distilling coal at relatively low temperatures. The low temperature distillation of coal yields a larger amount of oil, containing members of the paraffin and olefin series, than the ordinary or high temperature coking process and with further commercial development a considerable amount of motor fuel may be obtained from coal treated by the low temperature distillation process.

In 1916, 502,519,682 tons (2000 lbs. per ton) of bituminous coal were mined in the United States, together with 87,578,493 tons (2400 lbs. per ton) of Pennsylvania anthracite.

It is also estimated that in the same year 307,267,000 barrels of petroleum were produced in the United States. Assuming the arbitrary value of 0.889 as an average specific gravity of the crude oil produced, it follows that about 48,000,000 short tons, in round numbers, of oil were produced as compared with over 590,000,000 short tons of coal. **Arrhenius** estimates that the world's yearly production of mineral oils represents not quite three per cent of the energy contained in the yearly production of coal.

It would appear desirable that a method be evolved for converting a large percentage, say fifty per cent, of coal into liquid fuel. In this connection attention is directed to a process described in Chapter XXVIII whereby coal is converted into liquid fuel by treatment with hydrogen.

It is evident that coal is one of our largest sources of energy. Its

solidity is due mainly, speaking from a chemical standpoint, to the fact that it contains a larger percentage of carbon than is found in petroleum. Hydrogen appears to be the element which is needed to convert coal into liquid fuel resembling petroleum, as is shown by experiment. It may therefore not be idle to suppose that when more is known about the chemical constitution of coal and its reactivity in general methods may be found to secure a large yield of light hydrocarbons by suitable treatment. In these days of transportation difficulties, a method by which coal could be partly converted, at the mines, into liquid fuel, which could be pumped to points of consumption is, to say the least, desirable; and with the application of the necessary research and encouragement, it is believed by the authors that difficulties inherent in such a development are not insurmountable.

George H. Ashley, chief of the Topographic and Geological Survey of the Pennsylvania Department of Internal Affairs, in a report filed with James F. Woodward, secretary of the department, declares that the increased consumption of oil and gasoline in this country will necessitate the finding of additional sources of supply. He says that by proper treatment of 100,000,000 of the 180,000,000 tons of bituminous coal mined in this State each year the oil supply could be increased by more than 1,000,000,000 gallons.

The State geologist said in his statement that at the present time there is no decrease in the supply of oil and gasoline in the country, but that rather there has been a continuous increase in the production. However, he pointed out, during the last year the demand has exceeded the supply and the country's reserve stock has been reduced materially. It has been necessary, because of the exportation of gasoline, to import oil from other quarters. The initial production of oil in new wells has been far below the initial production of wells in years gone by, he contended. The increasing costs in machinery and operation and. a smaller initial flow, taken together with the ever increasing demands for gasoline, according to Ashley, are responsible for the higher prices.

In discussing the possibility of securing oil from bituminous coal, Ashley says: —

" Today, except for metallurgical purposes, we burn coal in a raw state, wasting, when used for power, from 80 to 95 per cent of the heat and energy in the coal and all of the oil, gas, tar and other by-products, except as they are burned in the fire. It may safely be predicted that the next ten years will see a revolution in our use of raw coal. Already the by-product coke oven is replacing the old bee hive oven. The coke is made by the distillation of bituminous coal at a high temperature, around 1200° F. (649° C.), the quantity of gas given off is

reduced and the coal is replaced by a smokeless fuel, called in one process ' coalite,' having the same heating value as an equal weight of coal and oil.   A plant operating in England with English coal is reported as obtaining from one ton of coal: — 3 gallons of motor spirits suitable for every purpose for which gasoline is used; 16 gallons of oil similar to crude petroleum which can be used for burning, light, lubricating or for 'distillation; 7000 feet of gas, richer in heat and higher in candle power than ordinary coal gas; 20 pounds of sulphate of ammonia for fertilizing and high explosives and 1400 pounds of smokeless fuel.

" Contrasting these figures with those showing the production from by-product coke ovens now operating in the Pittsburgh district, it should be noted that the coke ovens operating at a high temperature give only 1100 pounds of coke and no oil, but give 300 pounds of tar and only $6\frac{1}{2}$ pounds of ammonium sulphate, 3 gallons of benzol and 7000 feet of gas."

Benzol as a Motor Fuel

Foxwell [1] holds the view that the deposition of soot or carbon deposit on valve settings, cylinder walls and ignition devices which has sometimes occurred when benzol has been substituted for gasoline is due to an insufficient air supply.

This view is upheld by **Watson, Frost, Lloyd, Richards, Stern, Shaw** and **Wilson,** [2] who have given the matter thorough consideration.

The benzol used was similar in character to two samples purchased at different garages, and became practically solid at $- 12°$ C. ($10.4°$ F.); the first indication of crystallization occurred at $- 4°$ C. ($25°$ F.).   The crystals at once sink in the liquid, and risk of choking the jet of the carburetor, as well as that of impeding the flow of liquid, is incurred. Even if crystals do not separate, the viscosity of the liquid at low temperatures may be sufficiently increased to influence the supply of fuel. The viscosity of benzol increases at a greater rate than that of gasoline, and in cold weather it is important to heat the jet of the carburetor, or any constriction in the fuel-supply service.   A mixture of one part of gasoline to three parts of benzol starts depositing at $- 14°$C. ($6.8°$ F.) while a mixture of equal volumes of these liquids gives no deposit at $- 21°$ C. ($5.8°$ F.).   It would be advantageous to mix 30 per cent of gasoline with benzol.   The knocking produced at low engine speeds when gasoline is used as fuel is not observed with benzol.   This appears

[1] Chem. Abs. 1914, 1497; J. Gas Lighting, 125, 292–3.

[2] J. S C. I 1915, 266; Inst. Automobile Eng., December 1914; Proc. Inst. Automobile Eng. 7, 35.

to be due to the fact that the critical temperature above which the charge fires, in a way resembling detonation rather than inflammation, is much lower for gasoline. Benzol added to gasoline causes a marked increase in the critical temperature, and an engine which knocks badly with pure gasoline runs quite smoothly with a mixture of equal parts of gasoline and benzol. *When using less than twelve parts of air to one of benzol by weight the deposit of carbon in the engine is excessive, and the efficiency is greatly impaired. If the mixture is so adjusted that practically no carbon monoxide is found in the exhaust gases, the carbon deposit is no worse than with gasoline.*

The Petroleum Committee of the Royal Automobile Club [1] summarizes its conclusions on the applicability of benzol as motor fuel as follows:

Benzol properly manufactured gives an average of 15 per cent more mileage than gasoline and greater pulling power. The chief disadvantages are: (1) difficult starting in cold weather, (2) sooting of the valves, (3) objectionable exhaust.

A comparison between the power developed by gasoline, benzol and alcohol-benzol mixtures is given by **Ormandy.** [2] A four cylinder Mandslay engine with cylinders of 90 millimeter bore and 130 millimeter stroke and compression space about one-quarter of the total cylinder volume, was tested with different fuels with the following results:

Fuel used	Power Gasoline = 100	Vol of Fuel used. Gasoline = 100
	per cent	per cent
Gasoline	100	100
Benzol	98 25	84 5
Benzol (1 part) + methylated spirit (1 part) .	99	96 3
" " " " (2 parts) ..	92	108 9
" " " " (3 parts)	91 5	121.5

The specific gravity of the gasoline was 0.710 (67.1° Bé.) and of the methylated spirit 0.815 (41.8° Bé.). Two qualities of benzol were used, namely, 90 per cent, with specific gravity 0.885 (28.2° Bé.) and 50–90 per cent, with specific gravity 0.875 (30° Bé.). Both benzols gave, it is said, the same results when mixed with alcohol. In the above tests the engine was run at 1000 R.P.M.

[1] Chem Abs 1913, 1414; Gas World, 58, 175–6.
[2] J. S. C. I. 1913, 1096A; J. Gas Lighting, 1913, 124, 580.

A study of relative volatility of benzol (coal), gasoline, alcohol, aleohol-benzol mixtures, toluol and alcohol-benzol toluol mixtures has been made by **Meneghini.**[1] The method used consisted in aspirating a constant volume of dry air over a small amount of the liquid (contained in a U-tube in a thermostat at 25° C.) under a slight sub-atmospheric pressure (40 mm. of water). The difference in weight of the U-tube gave the amount of substance evaporated. Alcohol of 99, 95, 90 and 80 per cent respectively, gave 1.99, 1.90, 1.85 and 1.85 per cent of evaporation. Propyl alcohol gave 0.85 per cent, benzol
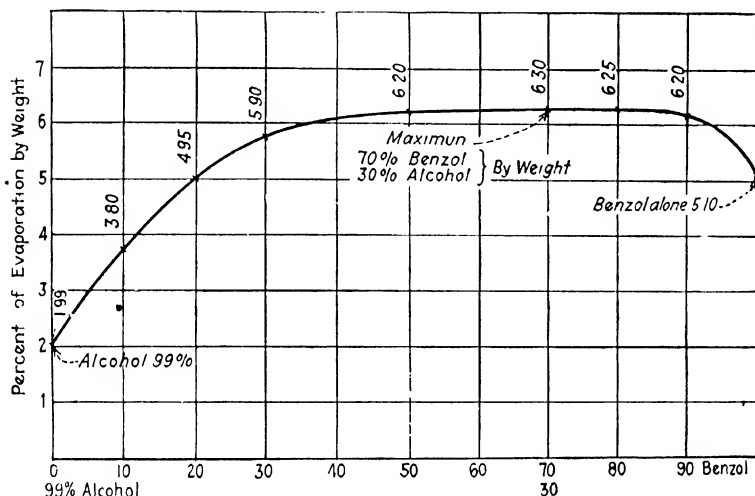
Fig. 199.

5.10 per cent, toluol 1.73 per cent. Alcohol-benzol mixtures containing by volume 10, 20, 30, 50, 70, 80, and 90 per cent, respectively, of benzol gave 3.80, 4.95, 5.90, 6.20, 6.30, 6.25, and 6.20 per cent. (The mixture of maximum volatility appears therefore to be that containing 70 per cent benzol and 30 per cent of alcohol by volume and this possesses a volatility greater than that of alcohol or benzol alone.) Addition of toluol to benzol-alcohol mixtures amounting to 10 per cent of the volume of the benzol does not, it is said, appreciably influence the velocity of evaporation.

For alcohol-toluol mixtures containing 10, 25, 50, 60, 75, 90 per cent, respectively, of alcohol the figures were 2.90, 3.15, 3.10, 2.95, 2.65, 2.25 per cent. Here the mixture of maximum volatility consists

[1] J. S. C. I. 1915, 603A; Annali Chim. Appl. 1915 [3], 235–244.

of about 25 per cent alcohol and 75 per cent toluol, although the rate of evaporation of this optimum mixture is only half that of the optimum alcohol-benzol mixture. See Figs. 199 and 200.

Benzol-toluol mixtures with 15, 30, 50, 70 and 90 per cent of benzol gave, respectively 2.50, 3.40, 4.30, 4.80 and 5.05 per cents of evaporation. Values obtained from commercial benzol, toluol and alcohol were practically the same as those given by the pure products. A commercial gasoline gave a value of 20.50 per cent [density = 0.700 (70° Bé.)].
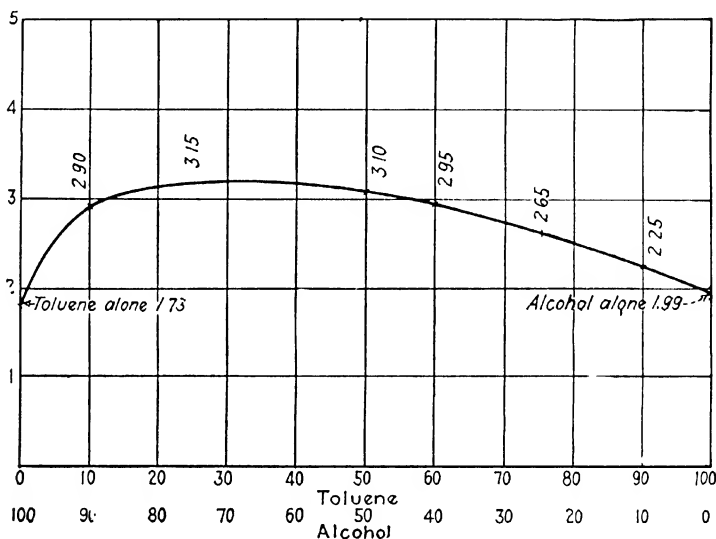
Fig. 200.

Since commercial benzol freezes at about − 5°C. (23° F.) **Dieterich-Helfenberg**[1] recommends a mixture of $\frac{1}{3}$ light petroleum naphtha (specific gravity 0.650) and $\frac{2}{3}$ commercial benzol. Such a mixture has the additional advantage of possessing a lower temperature of gasification than benzol alone.

A. Grebel[2] points out the necessity of careful washing of benzol and states that the poorly washed product corrodes the motor.

The following table gives certain physical constants for the fuels mentioned.

[1] Chem. Abs. 1914, 2618; Pharm -Post, 47, 183-9.
[2] Chem. Abs. 1909, 711; Le Génie Civil, 53, 113-6; Through Petroleum, 3, 1131.

	Sp. gr. 15.0° C.	Cal. per kg.	Cal per liter	Freezing Point	Boiling Point	Vap. Press. Mm. Hg. at 20° C.
Gasoline	0.700	11,464	8025	− 100° C.	50° C.	296
90 per cent benzol	0.885	10,033	8879	− 6 to − 8° C.	81° C.	122
Alcohol (denatured)	0 835	5,954	4971	− 100° C.	78.4° C.	51
Alcohol, carbureted with benzol . ..	0.854	7,874	6728	− 11° C.	67.0° C.	106

Attention is called to the fact that the boiling point of the alcohol-benzol mixture is lower than that of either alcohol or benzol alone.

A. Spilker [1] emphasizes the necessity for refining raw benzol with sulphuric acid before using it as motor fuel. Crude benzol is stated to contain material which causes clogging of the valves with resinous and pitchy matter, whereas refined 90 per cent benzol is free from this objection and constitutes an excellent substitute for gasoline. The residue from the evaporation of crude benzol which stood three months is reported to have been 1.86 gram per kilogram. Refined 90 per cent benzol, however, left no weighable residue on evaporation, even after standing three months. Cyclopentadiene is suggested as the source of the resinifiable matter. [2]

[1] J. S. C. I. 1910, 616A; Chem. Zeit. 1910 (34), 478–479.

[2] **Kraemer** and **Spilker**, J. S. C I. 1896, 443; Ber. 1896 (29), 552–561, have isolated a reactive hydrocarbon from crude benzene to which they have assigned the name cyclopentadiene

$$HC - CH$$
$$\| \quad \|$$
$$HC \quad CH$$
$$\diagdown \diagup$$
$$CH_2$$
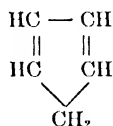
The first runnings from crude benzene or compressed gas oil formed the raw material for the investigation. It was soon observed that prolonged standing affected the boiling points of these oils in an upward direction. Careful fractionation of the light oils *thus changed*, yielded a liquid boiling at 160° to 175° C. (320°–347° F.), from which the hydrocarbon, named cyclopentadiene was isolated. It boils at 41° C. (106° F.) (corr.) under 760 millimeters' pressure, specific gravity 0.815 at 15°/15° C. (59° F.); it is insoluble in water, but miscible in every proportion with alcohol, ether and benzene. Concentrated sulphuric acid and nitric acid cause it to explode; dilute acids and alkalies resinify it. It reduces an ammoniacal silver solution containing potash and forms mono-, tri-, and tetrachloro compounds.

Dibromcyclopentene is obtained by combining cyclopentadiene, suspended in twice its weight of light petroleum, with the theoretical quantity of bromine at

F. W. Sperr,[1] in purifying heavy naphtha by treatment with acid and alkali, finds that it is more advantageous to dissolve the heavy naphtha in light naphtha (previously acid treated) and then to complete the chemical treatment of the solution, than it is to treat the heavy naphtha separately. The sticky polymerized products resulting in the latter case are thereby rendered more mobile and easy to handle.

Comparative analyses of the exhaust gas obtained with gasoline and a benzol mixture as motor fuel are given by **I. C. Mackie**[2] the tests being made at the same engine speed (about 17 miles per hour), and with various settings of the carburetor needle valve. The benzol mixture, termed "disco fuel," consisted of 72 per cent benzol, 21 per cent toluol, and 7 per cent solvent naphtha. For all ordinary settings of the needle valve the exhaust gases from the benzol tests contained more carbon dioxide, more free oxygen, and less carbon monoxide than those from the gasoline tests. Other tests were made to determine the effect of various adjustments of the cold air inlet to the carburetor, leaving the needle valve unaltered, and the results indicated that no alteration of carburetor was necessary in changing from gasoline to benzol mixtures. A test under extreme conditions, with the engine speed as before, in a garage heated to 110° F. (43° C.) and with the cold air inlet to the carburetor closed, showed that even under such conditions the combustion was more complete with the benzol, and the same conclusion was drawn from tests in which the speed of the engine was varied, and under actual driving conditions on the level and climbing a hill.

Mackie affirms that benzol is superior to gasoline as regards the power developed by the engine and the mileage obtained per gallon and has the further advantage that the spark lever can be left in the advanced position, even when the engine is at low speed, without the least trouble due to premature explosion. The one disadvantage of benzol fuels, as normally obtained from gas, Mackie considers is their rela-

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– 15° to – 20° C. (+ 5° to – 4° F.). It forms colorless crystals melting at 45° to 46° C. (113–115° F.), is readily soluble in benzene and chloroform, but decomposes per se or when treated with alcohol and water

It is maintained that the results obtained on chlorination and bromination confirm the correctness of the formula originally assigned by **Kraemer** and **Spilker** to cyclopentadiene, the discovery of which fills a gap in the indene series, thus:

$$C_2H_2'' - C_2H_2'' \qquad C_6H_4 - C_2H_2'' \qquad C_6H_4 - C_6H_4$$
$$\diagdown \diagup \qquad\qquad \diagdown \diagup \qquad\qquad \diagdown \diagup$$
$$CH_2 \qquad\qquad\quad CH_2 \qquad\qquad\quad CH_2$$

Cyclopentadiene   Indene   Fluorene
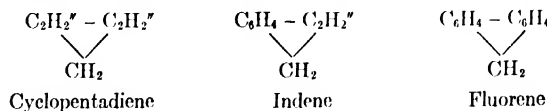
[1] U. S. Patent 1,246,671, Nov. 13, 1917.
[2] J. S. C. I. 1919, 808 A: Canadian Chem. J., 1919, 3, 295–297.

tively high freezing point. This may be obviated by blending them with sufficient gasoline (e.g. 50 per cent) to give a suitable winter fuel, or by the addition of a larger proportion of toluol or xylol to the benzol.[1]

W. Goslich [2] has determined the fuel economy resulting from the addition of benzol to alcohol and utilizing the mixture in a Körting's alcohol engine. Mixtures were used containing up to 30 per cent benzol by weight and the kilograms of fuel consumed per horsepower hour were determined and compared with the original fuel (86 per cent alcohol by weight). In all cases a fuel economy (by weight) was noted. The largest saving was observed in the mixture containing 20 per cent of benzol by weight. Here 0.37 kilos were consumed per horsepower hour as compared with 0.42 kilos for the alcohol, representing a gain of 12 per cent over the original alcohol fuel, under practically the same operating conditions, namely, speed 227 228 R.P.M. and a developed horsepower of 8.9. The observation is made that whether the fuel economy results in a financial gain depends upon the relative prices of alcohol and benzol.

Although the heating value of alcohol is lower than that of petroleum benzine it is claimed to be thermally more efficient in an internal combustion engine, 23 to 24 per cent of its heating value being utilized as against 14 18 per cent for petroleum benzine.[3]

Benzol and Motor Fuel from Coal

Benzol and toluol are closely allied substances. Benzol is either the pure substance benzene (C_6H_6) or a mixture containing benzene as one component. Benzol is graded commercially as crude or refined, and according to the percentage which distills below 100° C. (212° F.). Refined benzol has been washed with sulphuric acid and with alkali, a process which gives a colorless or " white " product. Crude benzol has not been so treated, and is apt to contain carbon bisulphide, thiophen, and probably pyridin, and to have a dark or straw color.

" Pure benzol " should be the pure substance benzene (C_6H_6), boiling point 80.5° C. (176.9° F.), melting point 5° C. (41° F.), specific gravity 0.884 at 15° C. with only traces of impurities.

The term " benzol," however, is also used in commerce and in tariff

[1] In Nova Scotia the use of benzol and solvent naphtha for motor fuel has been steadily increasing according to I. C. Mackie (J. S. C. I. 1919, 308 R.).

[2] J. S. C. I. 1900, 329; Zeits. Spiritusind. 1900 (23) (8), 65.

[3] J. S. C. I. 1901, 853; U. S. Cons. Reps. Vol. LXVI, No. 250, July 1901.

codes to describe mixtures containing benzene as one component.[1] For example, a " crude 90 per cent benzol " is a product of which approximately and at least 90 per cent distills below 100° C. (212° F.). It will contain about 70 per cent of benzene, 24 per cent of toluene, and 6 per cent of impurities of a different chemical nature.

Toluol is the pure substance toluene (C_7H_8) or a mixture containing toluene as one component. Toluol, like benzol, is graded as crude and refined and also according to the percentage distilling below 120° C. (248° F.). "Pure toluol " should consist of the substance toluene (C_7H_8) with only traces of impurities.

The impure grades are used chiefly as substitutes for turpentine (as a thinner for paints and varnish), in paint removers, and as a solvent for many organic substances. They can be used as a substitute for gasoline as a motor fuel whenever the prices are low enough.

During the war nearly all the available supply of toluol was marketed in the pure grade for the manufacture of explosives, dyes, and other chemicals. With the disappearance of the demand for explosives much of the toluol will be marketed in a less pure condition for use as a solvent or fuel.

Benzol and toluol are derived from coal tar, but these oils are obtained chiefly by removing or " stripping " them from coal gas and carbureted water gas. Before the outbreak of the European war, such stripping plants were not in general use but in recent years they have been installed at every by-product coke-oven plant in the United States and in many plants supplying illuminating gas for city distribution.

In addition small amounts have been secured by passing petroleum oil through red-hot iron tubes under pressure. The oil is thereby partly " cracked " into gasoline, benzol, toluol, and other products.

A certain amount has been secured by the distillation of crude petroleum oil of unusual composition found in California. As a general rule petroleum oil contains no benzol or toluol.[2]

The most striking fact brought out by statistics of the domestic supplies of crudes is the great increase in the output of benzol and toluol. In 1914 the production of crude light oils was 8,464,274 gallons, an amount sufficient for the production of about 4,500,000 gallons of benzol and 1,500,000 gallons of toluol. In 1917 the output of benzol

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[1] United States Tariff Commission Report on Dyes and Related Coal Tar Chemicals (1918).

[2] The commercial isolation of toluene from petroleum spirit in the form of its mononitro derivative has also been a feature of the late war. Vast amounts of TNT have been manufactured from this source, and, it is asserted (J. S. C. I. 1920, 3R) to a large extent this operation was a deciding factor in the struggle.

was 40,192,930 gallons and of toluol 10,219,830 gallons. In 1918 the output of benzol is estimated to have been over 52,000,000 gallons, and of toluol about 14,000,000 gallons. The increase in output is due primarily to the need for these materials for the explosive industry during the war. It is estimated that 95,000,000 gallons of benzol will be produced in this country in 1920 and that this will represent only about two per cent of the gasoline supplies for the year.[1]

Now that the military demand for these products for the manufacture of explosives has disappeared, the productive capacity of the plants is far in excess of the requirements for the manufacture of dyes and other chemical products. Benzol and toluol find important uses as solvents, especially in paints. They can be used as fuel for internal combustion engines either alone or mixed with gasoline or alcohol. The price of benzol and toluol may therefore be expected to decline until it is profitable to use them for fuel in competition with gasoline. A similar condition will exist in England and Germany. However, the United States, being the largest producer and exporter of gasoline, should have the lowest price for gasoline of any nation and, therefore, the lowest price for benzol and toluol.

Previous to the war very little attention was paid in France to the production of pure benzene and toluene[2] but the requirements

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[1] It is estimated that France requires at least 176,000,000 gallons of motor spirit annually, and before the war some 19,000,000 gallons of benzol, mostly imported, were used for internal combustion engines. To the continuance of the recovery of benzol at gas works and to the extension of the recovery at coke works, France must look to supply the want. The possibilities of improvement and economy in the treatment of the benzol-laden wash oil are considerable. Crude benzol is recovered from the wash oil by the aid of direct and indirect steam. If the products from the debenzolizing still are all condensed together, the greater part of the heat in the indirect steam is lost, and it is suggested that the vapors coming from the still should at once, and without condensation, be submitted to a process of fractional separation. This was first proposed by Mallet and has been carried out at Lens, Auby and Sluiskill. The process consists in passing the vapors from the debenzolizing still through two or more rectifying dephlegmating columns in succession. By this means a high yield of specially pure intermediate products is obtained and less chemicals are required for washing. Berthelot considers that the fractionating column with bubbling trays is likely soon to be replaced by contact columns and insists on the importance of the dephlemator, which, especially for the final rectification, should be capable of returning to the column as liquid four-fifths of the vapor which enters it. The function of the dephlegmator is not to hold back the vapor of the less volatile liquids, but to provide return liquid for the column. This return liquid should enter the fractioning column about halfway up. The use of a vacuum for the fractionation of the higher boiling products is not warranted by experience. (C. Berthelot. Cnim. et Ind., 1919, 2, 1017; J. S. C. I. 1919, 942A.)

[2] A. Baril. Chim et. Ind., 1919, 2, 1013-1016; J. S. C. I. 1919, 942A.
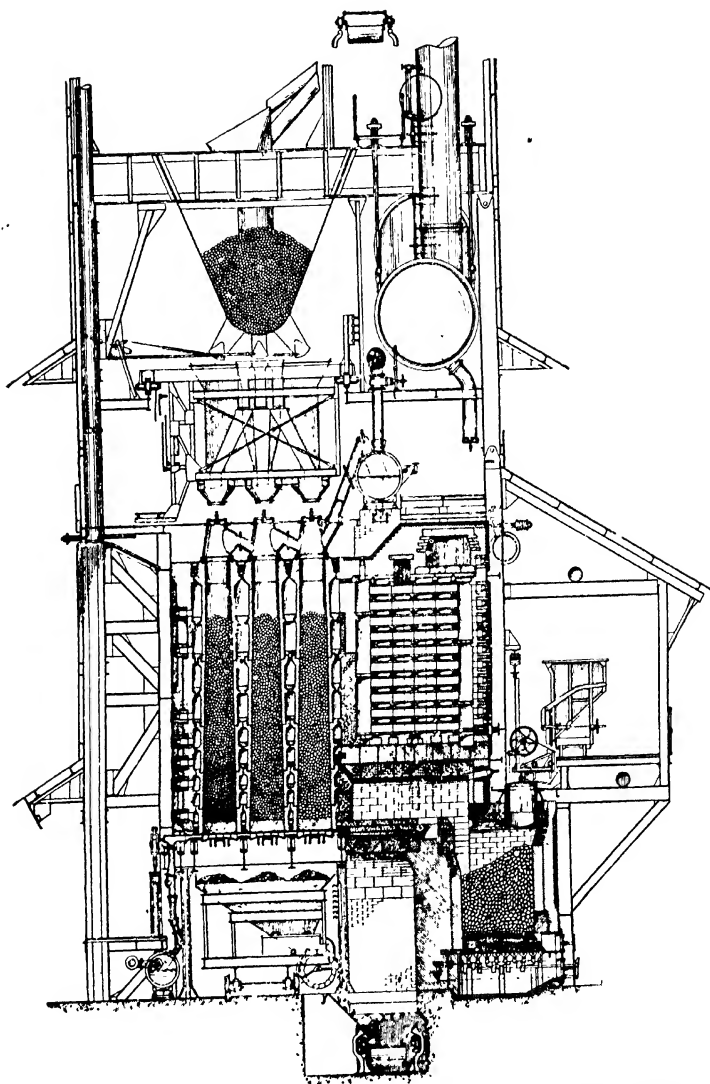
Fig. 200a. — The United Gas Improvement Company Vertical Retort System.
(Sectional elevational view).
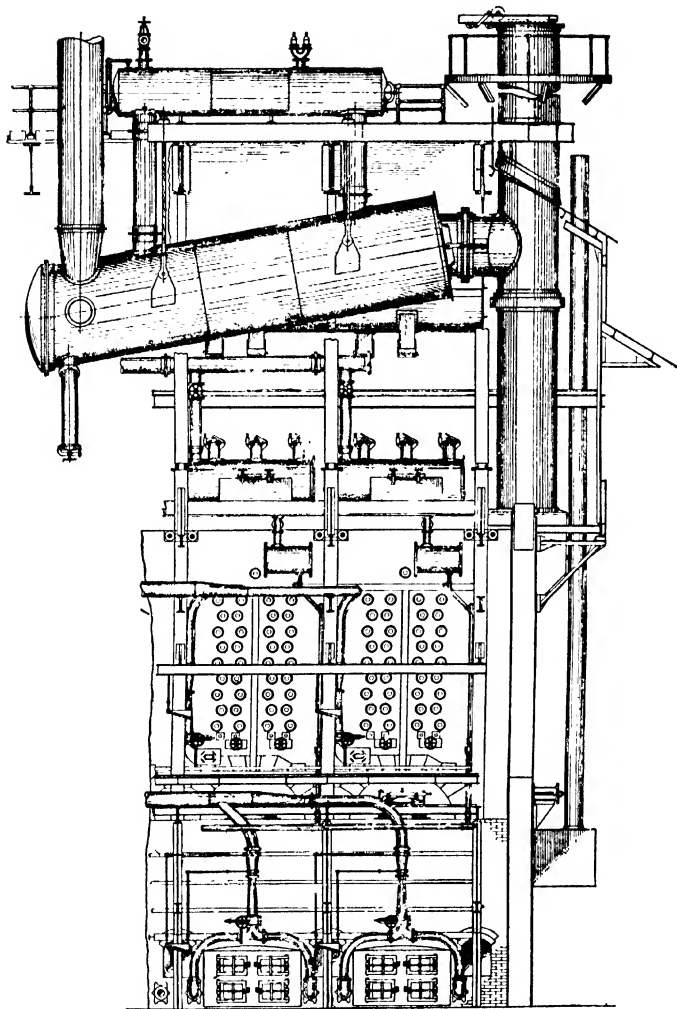
Fig. 200b. — The United Gas Improvement Company Vertical Retort System. (Front elevation).

of the Explosives Department during the war enforced the production
of these products at the Paris gas works. Formerly the intermittent
system of rectification was employed, and this necessitated a consider-
able number of operations to obtain pure products, and the loss in
handling was considerable. A continuous system was therefore adopted,
namely, that of Egrot et Grange, which consists of three-column stills
set in cascade, each having its own dephlegmator and condenser.
Crude benzol was fed into the uppermost column and passed through
the others in succession. The carbon bisulphide and low-boiling im-
purities were removed by the first column, pure benzene distilling
within 0.5°–0.7° C. was obtained from the condenser of the second,
pure toluene of a similar degree of purity from the third and solvent
naphtha containing only a trace of toluene was discharged from the
bottom of the third still. The apparatus, which worked with great
regularity and gave very little trouble, was able to treat from 35 to 42
tons of washed crude benzol per 24 hours, using only about $\frac{5}{8}$ of the
amount of steam required to effect the same degree of separation in an
intermittent apparatus.

The chief commercial sources of benzol and toluol are coke-oven
gas, carbureted water gas, coal gas and oil gas. The tar which results
from the coking of coal and from the decomposition of pettoleum oil
in carburetors of water gas plants and in the manufacture of oil gas
also contains light oil, including benzol and toluol, but these hydro-
carbons remain for the most part in the gas.

H. C. Porter [1] observes that high-grade gas coal yields nearly 1 per
cent of " gas benzol " by weight, the value of which in the crude state
is in the neighborhood of 20 per cent of that of the coal; the light
oil of tar, on the other hand, constitutes only 0.1 to 0.2 per cent of
the coal.

A practice quite common in many cities of the United States consists
in operating a carbureted water gas plant and a coal gas plant in con-
junction with each other and mixing the resultant gases. This practice
comprises certain economies in plant operation. On the Pacific coast,
where coal is relatively expensive as compared with oil, the manufacture
of oil gas is common. This process consists in spraying a mixture of
oil and steam onto highly heated checker bricks, the latter having been
previously heated by hot gases resulting from the combustion of oil.

The following table gives the approximate yields of crude light
oil and the composition of the latter obtained from the several varieties
of gas.

¹ Bureau of Mines Technical Paper 89 (1915), p. 5, " Coal Tar Products."

Table 5. — Approximate Yields of Crude Light Oil and Pure Products and Approximate Composition of Crude Light Oil [1]

Approximate Yield of Crude Light Oil

Kind of gas	Yield
Coal gas:	
Horizontal retort	3.0–4.0 gallons per short ton coal carbonized
Continuous vertical retort [2]	1 5–2.5 gallons per short ton coal carbonized
Inclined retort	1.8–2.3 gallons per short ton coal carbonized
Coke-oven gas, run of oven. . .	2 6–3.6 gallons per short ton coal carbonized
Carbureted water gas	8–10 per cent of volume of gas oil used
Oil gas.	0 2–0 3 gallons per 1000 cubic feet of gas

Approximate Composition of Crude Light Oil

	Benzol	Toluol	Solvent naphtha, wash oil, naphthalene, etc.
Coal gas:	Per cent	Per cent	Per cent
Horizontal retort	50	13–18	35
Continuous vertical retort [3] . . .	30	10–15	55
Inclined retort	45	13–18	40
Coke-oven gas, run of oven	50	14–18	35
Carbureted water gas	40	20–25	37
Oil gas	80	8–10	10

Approximate Yield of Pure Products

	Benzol	Toluol
Gallons per short ton coal carbonized:		
Coal gas:		
Horizontal retort	1.5	0.4 –0.5
Continuous vertical retort [2]	.6	.2 – .3
Inclined retort	.9	.2 – .4
Coke-oven gas, run of oven	1.5	.3 – .5
Gallons per 1000 cubic feet of gas:		
Carbureted water gas [3]	.15	.06– .10
Oil gas	.25	.02– .03

[1] Bureau of Standards, Technologic Paper No. 117, by McBride, Reinicker and Dunkley.

[2] Information from only one continuous vertical retort installation included here.

[3] The yield of toluol is variable according to amount of oil used in manufacturing the gas, being equivalent to about 2.0–2.2 per cent of the gas oil used in the plants investigated, but perhaps only about 1.6 per cent in many cases.

It will be noted that, according to Table 5, as regards the composition of the light oil condensed from the various gases, that from oil gas contains the largest proportion of benzol, with coke-oven and coal-gas light oils following, while the light oil from carbureted water gas contains a larger proportion of toluol than occurs in the other varieties of condensate.

Removal of Light Oils from the Gas[1]

To recover light oils from the gas the method now almost universally employed is to bring the gas into contact with a medium which has a solvent action upon the light oils. In any case to obtain complete absorption it is necessary that an adequate amount of the washing medium be brought into contact with the gas at a sufficiently low temperature. The temperature usually should not exceed 30° C. (86° F.). The temperatures obtainable in practice will, of course, depend upon the facilities available for cooling the gas and the washing oil. It is desirable to have the oil a little warmer than the gas to prevent condensation of water from the gas into the oil, which gives trouble in the further stages of recovery. The amount of washing medium circulated through the washers will depend upon the amount of light-oil vapors present in the gas, the temperature of the washing medium, the amount of gas to be washed, and the saturation of the washing medium which it is feasible to obtain. About 10 gallons of wash oil per 1000 cubic feet of gas washed seems to be an average figure.

The washing medium now usually employed for this purpose in this country is a petroleum distillate called from its color "straw oil." Some plants use a creosote oil obtained from the distillation of coal tar. The choice seems to depend largely upon which is available in a given case. The qualifications which a wash oil should possess seem to be substantially as follows:

A creosote oil upon distillation should yield not to exceed 5 per cent up to 200° C. and not less than 90 per cent between 200° and 300° C. The oil should not contain more than 7 per cent naphthalene and should not show any marked increase in viscosity down to 4° C. The oil should be as fluid as possible under the working conditions and should have as small capacity for heat as possible.

The characteristics of a straw oil for this purpose, as recommended by some operators and which are concurred in by the committee of coal-tar products, are substantially as follows:

1. Specific gravity not less than 0.860 (34° Bé.) at 15.5° C. (60° F.).
2. Flash point in open cup tests not less than 135° C. (275° F).
3. Viscosity in Saybolt viscosimeter at 37.7° C. (100° F.) not more than 70 seconds.
4. The pour test shall not be over − 1.1° C. (30° F.).

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[1] Bureau of Standards, Technologic Paper 117.
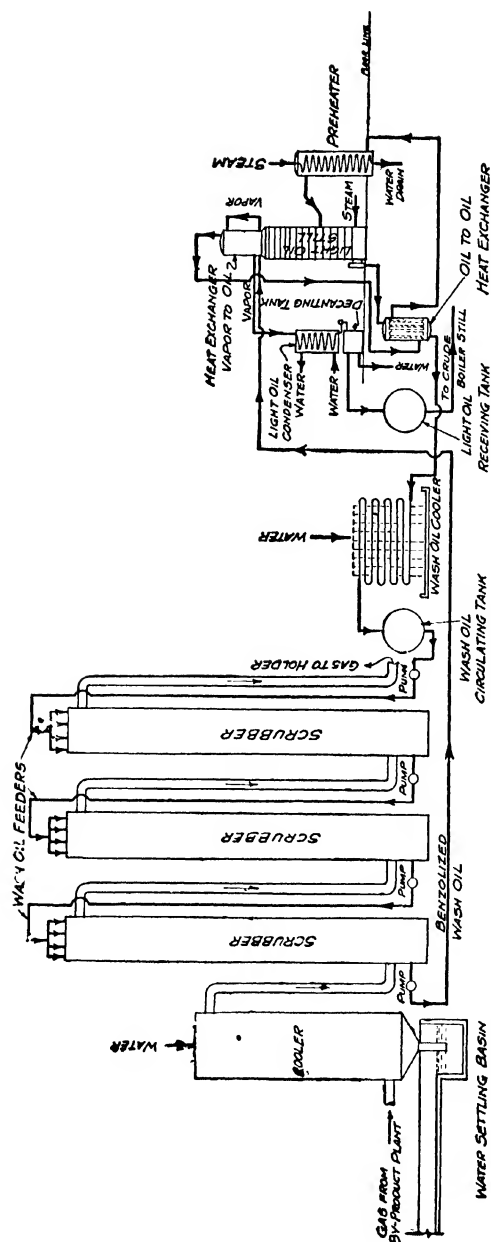
Fig. 202. — Diagram of light oil recovery from coke oven gases. From Roger's Manual of Industrial Chemistry page 562.

5. When 500 c.c. of the oil are distilled with steam at atmospheric pressure collecting 500 c.c. of condensed water, not over 5 c.c. of oil shall have distilled over.

6. The oil remaining after the steam distillation shall be poured into a 500 c.c. cylinder and shall show no permanent emulsion.

7. The oil shall not lose more than 10 per cent by volume in washing with two and one-half times its volume of 100 per cent sulphuric acid, when vigorously agitated with acid for five minutes and allowed to stand for two hours.

Some operators claim to have successfully used ordinary gas oil, water-gas tar, or coal tar. Other operators, however, state that when gas oil is used, the paraffin and olefin compounds in it are likely to contaminate the light oil and that on account of emulsification, this oil soon becomes unfit for use. Water-gas tar if used more than once may soon become too thick for use and also may lead to serious naphthalene deposits in the distribution system.

The advantages claimed for tar as a washing medium are briefly as follows: (a) The reduction in the investment in wash oil; (b) the elimination of delays from shortage of wash oil; (c) the direct recovery (without separate distillation) of the toluol and carbolic oils originally present in the tar; and (d) the elimination of those troubles caused by accumulation of naphthalene in the washing medium during repeated use, which troubles do not occur with the use of tar since it is not used more than a few times. It is sometimes claimed that tar need be used only once; but, on the other hand, it is pointed out by the opponents of the tar-washing process that since in coal-gas manufacture there are only about 10 gallons of tar produced per ton of coal carbonized and from 2.5 to 4 gallons of light oil, if tar were used for washing the gas and employed but once it would have to absorb from 25 to 40 per cent of its own volume of light oil in one operation. Likewise in water-gas manufacture, each gallon of gas oil produces only about 0.15 to 0 2 gallon of tar and about 0.1 gallon of light oils. To use the tar but once would therefore require an absorption of about one-half to two-thirds of its volume of light oil. An absorption to such an extent is a physical impossibility. In fact, an enrichment of the washing medium greater than perhaps 2.5 to 3 per cent in coal-gas practice or of 4 to 5 per cent in water-gas practice is not desirable, since serious losses are likely to occur.

Stripping the Wash Oil [1]

To separate the light oils from the wash oil in which they are dissolved, some form of still is employed. The difference in boiling points makes possible the separation. In small plants either continuous or intermittent stills may be used. The separation of light oils from the benzolized wash oil should be nearly complete. It is stated that good operating practice will leave only from 0.1 to 0.3 per cent of oils distilling below 200° C. in the debenzolized oil. In large plants there are used continuous stills in which steam comes in contact with the wash oil and boils off the light oils. The light-oil vapors, together with the uncondensed portion of the steam, ascend through a series of chambers. In their ascent they come in contact with descending wash oil carrying

[1] Bureau of Standards, *loc. cit.*

light oils which they assist in freeing. The light-oil vapors, together with some steam, naphthalene, sulphur compounds, etc., pass away from the still and are condensed. Some operators advise the use of steam sufficiently superheated so that nearly all of it leaves the still uncondensed with the light-oil vapors.

In plants stripping water gas, trouble is experienced by the separation from the wash oil of polymerization products of a gummy nature, and provision should be made for the settling and removal of this sludge from the wash oil. Suitable provision should also be made to remove any water that separates from the wash oil at the scrubbers and in the circulating tanks, since water not only interferes with the operation of the stripping still but also lessens the absorption of light oils from the gas. The principal sources of this water are: (a) The mist carried forward with the gas when direct gas coolers are used; (b) condensation from the gas when the temperature of the wash oil is lower than that of the gas; (c) wet steam supplied to the stripping still; and (d) condensation from the direct steam supplied to the stripping still when the temperature of the benzolized oil leaving the superheater is too low.

Refining [1]

To obtain from the light oils those constituents which are in most demand, a further separation by distillation and chemical treatment is necessary. The light oil is distilled in some form of still, usually equipped with a rectifying column and dephlegmator. The latter apparatus acts as a partial condenser in which part of the vapor is condensed and, falling downward through the rectifying column, meets the ascending vapors and washes from them a portion of the high-boiling constituents. Only the light low-boiling constituents are able to pass the dephlegmator uncondensed. What vapors shall be allowed to pass on to the condensers depends upon the temperature maintained at the dephlegmator. This temperature is regulated according to the particular oil which it is desired to separate from the light-oil mixture at any particular stage of the distillation. By the use of the dephlegmator and rectifying column, it is possible to obtain much more definite separation of the benzol, toluol, and other aromatics than would otherwise be possible. In making the first distillation of the light oil, it is usual to collect the distillate in three successive portions or fractions, making the " cuts " at predetermined temperatures. The first fraction is collected in a containing vessel or receiver until the temperature at the top of the still is 100° C. (212° F.). This fraction is called crude

[1] *Ibid.*

benzol, since benzol is its chief constituent. The flow of distillate is then diverted into another receiver and collected until a temperature of 120° C. (248° F.). is reached. This fraction is termed crude toluol, from its chief component. The fraction collected above 120° C. (248° F.) is called crude solvent naphtha, from the use to which it is put, as a solvent of various materials. The boiling points of pure benzol and pure toluol are about 80° C. (176° F.) and 110° C. (230° F.), respectively. It will be noted that one of the changes of fractions or cuts is made midway between these boiling points, while the boiling point of pure toluol is midway between the other cuts.

The above procedure is not universal. Some operators collect the crude benzol and toluol together and subsequently separate them. Some of the impurities present in the crude fractions have boiling points so close to those of benzol and toluol that they cannot be separated from them by distillation. To remove a certain class of these compounds, the unsaturated hydrocarbons, the fractions are washed successively with strong sulphuric acid, caustic soda, and water. The unsaturated compounds form a thick, tarry mass which settles out by gravity upon standing and is drawn off. The fractions are then redistilled in stills with more efficient rectifying columns than those used for the crude distillation, and fractions are finally obtained which boil within a single degree of the temperatures which have been determined as the boiling points of pure benzol, toluol, etc.

Supply of Coal Suitable for By-Products Manufacture. — In addition to the coal remaining in the great fields of coking coal in western Pennsylvania, which produce over 60 per cent of the coke made in the United States, this country has, it is stated, an entirely adequate source of tar, benzol, and other by-products in the coking coals of other districts. Coal fields in West Virginia, Virginia, and eastern Kentucky may be drawn on, if necessary, for much more coking coal than they now produce. Most of the western Pennsylvania coals, if coked in by-products ovens, will yield good coke and by-products, so that on the basis of the supply of high grade coking coal available there seems to be no reason why the use of by-product ovens should not be extended so as to yield whatever tar and benzol are required.

Oil and water-gas tars formed from the petroleum used in the manufacture of gas were produced in the United States in 1912 to the amount of 33,930,000. gallons.[1] These tars are thinner than ordinary coal tar but contain many of the same constituents, such as benzene, toluene, xylene, naphthalene, and anthracene, in smaller proportions, and may contribute a little to the raw material of some of the refined products described below, as the demand for raw materials increases.

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[1] Bureau of Standards, Technologic Paper 117, p. 10.

G. Stevenson [1] refers to the observation that limestone when intimately mixed with coal rich in hydrocarbons and with a high oxygen content, commences to decompose at a temperature lower than that of the resinous and other matter contained in the coal and that the actions taking place slightly retard the evolution of gases generally given off so freely with low grade coals and thus allows of their becoming more stable.• The coke is less soft and friable; the naphthalene is reduced; there is a marked reduction in the total sulphur content of the gas and a small reduction in the quantity of breeze; the ash is increased by 2 per cent; the tar is thinner and more oily with slight increase of yield; benzene and toluene were claimed to be greatly increased. The net result, it is said, proves that the increased quantity of gas alone paid the whole of the cost.

Motor Fuel from the Products of the Low Temperature Distillation of Coal. — The low temperature carbonization of coal has been studied by **Taylor** and **Porter**,[2] both historically and experimentally.

It is stated [3] that •Wheeler and his associates in England have carried on an extensive series of destructive distillations of coal chiefly with a view to its bearing on the process of ignition or inflammation of coal dust suspended in air. In the first experiments coal [4] was distilled from a small platinum retort at fixed temperatures ranging from 450° to 1100° C, the gases being collected at atmospheric pressure. Yields of tar, gas, and residue were determined From these experiments it was concluded that coal has a well-defined decomposition point between 700° and 800° C which corresponds with a marked increase in the quantity of hydrogen evolved. In a continuation of the same work,[5] coal was distilled from the same apparatus as before, the gas being collected in 5-second intervals, to obtain data on the rate of evolution and the composition of the several fractions Coal was also distilled in a vacuum, fractions being collected at 50° intervals up to a temperature of 650° C.

The conclusion drawn was that coal probably consisted of two main types of compounds — one more unstable and yielding mostly paraffin hydrocarbons; the other decomposing with greater difficulty and yielding mostly hydrogen In further support of this view, **Clark** and **Wheeler** [6] separated coal into two parts — a pyridine extract and an insoluble residue. Distillations were made on the original coal, extract, and residue By the use of chloroform as an additional

[1] Chem. Abs. 1916, 1704; Gas World, 1916 (64), 286 7; J. Gas Lighting 1916 (133), 692–3.

[2] Bureau of Mines Technical Paper 140 (1916). The Primary Volatile Products of the Carbonization of Coal.

[3] Ibid. pp. 48–50.

[4] Burgess, M. J., and Wheeler R. V., The volatile constituents of coal: Jour. Chem. Soc. vol. 97, 1910, pp. 1917–1935.

[5] Burgess M. J., and Wheeler R. V., The volatile constituents of coal: Jour. Chem. Soc. vol. 99, 1911, pp. 650–667.

[6] Clark A. H., and Wheeler R. V., The volatile constituents of coal: Jour. Chem. Soc. vol. 103, 1913, pp. 1705–1715.

solvent, the coal was separated into " humus " and " resinous " substances. The " humus " bodies were regarded as degradation products of cellulose and as being responsible for hydrogen in the gaseous volatile matter.[1] In general, the conclusions arrived at by Taylor and Porter [2] do not accord with the views of Wheeler as to the relative ease of decomposition of the two classes of constituents in coal.

Distillations of a larger quantity of coal (1 to 2 kilos) in a vacuum were also made in Wheeler's laboratories, for gases [3] and liquid products,[4] at temperatures below 500° C. The low-temperature tar consisted of about 50 per cent pitch and 50 per cent of oil, distilled from the tar at temperatures below 300° C. The composition of the oil was as follows: Ethylenic hydrocarbons, 40 to 45 per cent; phenols (chiefly cresol and xylenols), 12 to 15 per cent; aromatic compounds, 7 per cent; a small amount of solid paraffin hydrocarbons; traces of pyridine bases; no benzene, anthracene, carbon disulphide, or solid aromatic hydrocarbons.

Pictet and **Bouvier** [5] obtained by distilling coal in a partial vacuum at 450° C. a thin tar containing apparently no phenols, naphthalene, anthracene, or other aromatic compound.

Vignon [6] fractionally distilled several types of coal and found that paraffin gases predominated below 600° and hydrogen above 800° C.

Rau and **Lambris** [7] have conducted a thorough investigation of the formation of water in the destructive distillation of fuels. They found that more water was produced by slow heating than by rapid heating. Fuels of greater maturity produced less water than younger, less altered fuels.

Parr and **Olin** [8] treated Illinois coal with superheated steam, temperature 400° to 450° C., and obtained a yield of tar nearly equal to that of high-temperature carbonization; the gas yield was less than 10 per cent. Seventy per cent of the tar boiled below 240° C. and contained little free carbon. In a more recent report of the same authors [9] a good semicoke was described, which was made at 400° to 500° C. by a similar process. The tar produced contained only 30 per cent pitch with little free carbon. The oils were high in tar acids, but contained no naphthalene or anthracene.

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[1] For discussion, see Porter H. C., and Taylor G. B., The mode of decomposition of coal by heat: Proc. Am. Gas Inst. vol. 9, 1914, p. 238.

[2] *Ibid.*

[3] Burgess, M. J., and Wheeler R. V., The distillation of coal in a vacuum: Jour. Chem. Soc. vol. 105, 1914, pp. 131–140.

[4] Jones, D. T., and Wheeler R. V., The composition of coal: Jour. Chem. Soc. vol. 105, 1914, pp. 140–151, 2562–2565.

[5] Sur la distillation de la houille sous pression réduite (Distillation of coal under reduced pressure): Compt. rend. t. 137, 1913, pp. 779–781; Gas World, vol. 60, 1914, p. 45; Ber. Deut. chem. Gesell, Jahrg. 46, 1913, pp. 3342–3353

[6] [Fractional distillation of coal]: Compt. rend t 155, 1912, pp. 1514–17; Jour. Gas Lighting, vol. 121, 1913, p. 107; J. S. C. I. 1913, 76.

[7] Formation of water in the dry distillation of fuels: Gas World, vol. 59, 1913, p. 239; Jour. Gasbel. Jahrg. 56, 1913, pp. 533, 557, 589.

[8] Coking of coals at low temperatures: Univ. Illinois Eng. Exp. Sta. Bull. 60, 1912, p. 12; Jour. Gas. Lighting, vol. 122, 1913, pp. 533–535, 595–598.

[9] The coking of coal at low temperature with special reference to the properties and compositions of the products: Univ. Illinois Eng. Exp. Sta. Bull. 79, 1915, pp. 29–30.

Lewes[1] gives the composition of the tar from a low-temperature industrial operation. It contained an abundance of light solvent oils, small percentages of aromatic compounds and phenol, a high percentage of cresols, etc., no naphthalene, a small percentage of anthracene, and less than 2 per cent of free carbon.

The thermal effects of carbonization have recently been investigated by **Hollings** and **Cobb**.[2] They found that cellulose showed a strong exothermic reaction at temperatures of 345° to 400° C.; lignite showed the same effect, but it was less marked; and older coals, which have lost much of their cellulosic constituents, showed it scarcely at all. At temperatures between 600° and 800° C. all the types of coal tested displayed exothermicity; above 800° C. the process was neutral or slightly endothermic. Thermal effects at lower temperatures were only marked · in coals of high oxygen content.

The Primary Decomposition Processes.[3] — A high-grade bituminous coal of the gas-making type decomposes by heat primarily into paraffin hydrocarbons and a completely altered nonvolatile residue, with small quantities of water, carbon dioxide and carbon monoxide. The three latter products are the first produced, although in small quantity; from some other types of bituminous coal they are produced in greater relative quantities than from the gas-coal type. Complex and varied secondary reactions induced by superheating the hydrocarbons, water vapor, and carbon dioxide are of great importance in industrial high-temperature carbonization.

The products of low-temperature carbonization from coal of the Pittsburgh type on an industrial scale at about 800° to 900° F. (427° – 482° C.) will consist of a rich gas amounting to 0.6 to 0.7 cubic foot per pound of coal, and a large yield of oil, or tar, comprising 10 to 12 per cent of the coal. This tar consists chiefly of paraffin hydrocarbons, is very low or possibly entirely devoid of benzene and naphthalene derivatives and practically devoid of free carbon. The gas will contain 6 to 7 per cent of unsaturated hydrocarbons and 20 to 25 per cent of ethane and its higher homologues, and consequently will have a high calorific and illuminating value. The tar may be either redistilled or subjected to cracking processes so as to produce light oils — gasoline substitutes — whose yield will be greater than, and probably at least double, that obtained by high-temperature carbonization.

The results suggest the possibility that low-temperature carbonization might be utilized in gas manufacture as an enriching process by passing through the low-temperature retorts a relatively large quantity of a thin gas such as " blue-water gas," sweeping out the light oil vapors

[1] Carbonization of coal: Iron and Coal Trades Rev. vol 83, 1911, p. 1011.

[2] Thermal study of the carbonization process: Jour. Chem. Soc. vol. 107, 1915, p. 1106.

[3] **Porter,** *loc. cit.* p. 50.

that are primarily liberated at these low temperatures. The utilization of inferior coals for making gas by such a process may be found practicable, it is stated.

David Trevor Jones[1] summarizes his conclusions regarding the thermal decomposition of low temperature coal tar as follows:

(1) Ordinary coal tar is formed from coal at high temperatures chiefly as the result of the decomposition of a tar previously formed at low temperatures.

· (2) The mechanism of this process consists essentially in the decomposition of the naphthenes, paraffins, and unsaturated hydrocarbons present in the low temperature tar to form olefins of varying carbon content which condense at higher temperatures to aromatic substances.

(3) The gaseous olefins are at a maximum at 550° C. (1022° F.), the curve descending to a minimum at 750° C. (1382° F.), when they virtually disappear. Their disappearance at 750° C. (1382° F.) synchronizes with the appearance of naphthalene, and immediately precedes a rapid increase in the evolution of hydrogen.

(4) Hydrogen is formed at middle temperatures chiefly as the result of the decomposition of naphthenes. The increase at higher temperatures must probably be attributed to the union of aromatic molecules and to intramolecular ring closing.

(5) Phenols are primary products of coal distillation.[2]

(6) Benzene and its homologues are chiefly formed as the result of olefinic condensation. To some extent they are secondary products of coal distillation, having been formed by the thermal dehydrogenation of the corresponding naphthenes.

(7) Acetylene plays an insignificant part in coal tar formation. .

Decomposition of Coal-Tar Oils

W. H. Gartley[3] cracks solvent naphtha by distilling under a pressure of about 35 pounds per square inch. Distillation is continued until the gravity of the residue is about 28° Bé., when the gravity of the original naphtha was 30°–35° Bé. This residue is then distilled under atmospheric pressure, to coke, or down to heavy residuum and the distillate put back into the pressure still. It is said that in this way, the content of toluol in the crude naphtha is raised from 3 to 15 per cent.

C. M. Alexander[4] states that in cracking solvent naphtha, to pro-

[1] J. S. C. I. 1917, 7.   [2] Cf., however, Pictet, *loc. cit.*
[3] U. S. Patent 1,225,237, May 8, 1917.
[4] J. S. C. I. 1917, 922; U. S. Patent 1,230,975, June 26, 1917.

duce benzol and toluol, operation at atmospheric pressure gives very good results. Creosote oils, treated similarly, are said to yield low boiling phenols.

The temperatures used for solvent naphtha are around 800° C. (1472° F.) in a vertical retort. The time factor is said to be important, the rate of feed being such that at least 70 per cent by volume of the original oil is obtained as condensate, and of this, about 30 per cent should be high boiling oil like the original naphtha. Of the condensate, about 20-25 per cent will boil, it is said, from 75° to 130°·C.. (167° 266° F.).

O. B. Evans[1] uses heavy coal tar naphtha to carburet water gas, and by washing the carbureted gas and passing it through a condenser a condensate is collected, which (when the crude naphtha contains about 3 per cent toluol) contains about 13 per cent toluol.

R. L. Hill[2] subjects solvent naphtha to a temperature of about 600° C. (1112° F.) under pressure in a retort in the presence of a carbide (calcium carbide or barium carbide). Condensation also takes place under pressure. It is stated that the action of the carbide gives rise to increased yields of benzene and toluene.

The Manufacture of Benzol and its Homologues from Petroleum

By distilling the naphtha and burning oil fractions of Coalinga (California) petroleum through a column packed with stones (the height of the column being very great in proportion to the size of the still) **Frasch**[3] reports having isolated considerable amounts of aromatic hydrocarbons, from benzene (benzol) up to and including naphthalene.

The presence of benzene homologues in the high boiling distillates of petroleum is indicated by the work of **Brooks** and **Humphrey.**[4] The cracking of the heavier portions of Jennings and Oklahoma petroleum oils boiling above 275° C. (527° F.) by distillation at temperatures not exceeding 420° C. (788° F.) and pressures not exceeding 100 lbs., yields, it is said, benzene, toluene, and m-xylene in small quantity, and the same hydrocarbons were detected in the light oil obtained by heating Oklahoma oil with aluminum chloride. From paraffin wax no aromatic hydrocarbons were obtained and the distillates were not fluorescent; a synthetic phenyl-paraffin, on the other hand, made by condensing pure benzene with chlorinated paraffin

[1] U. S. Patent 1,230,087, June 12, 1917.
[2] U. S. Patent 1,269,439, June 11, 1918.
[3] U. S. Patent 968,760, Aug 30, 1910.
[4] J. S. C. I. 1916, 347; J. Amer. Chem. Soc. 1916, (38), 393–400.

wax in presence of aluminum chloride, gave highly fluorescent distillates and both benzene and toluene on cracking. This supports the view previously advanced by Brooks and Humphrey [1] that the fluorescence of petroleum oils is attributable to the presence of aromatic derivatives. Since in these cracking experiments the temperatures were too low to admit of the profound decomposition of the hydrocarbons into acetylene from which aromatic substances could then afterwards be synthetically produced, the conclu ion is drawn that the aromatic nuclei were present in the heavy high boiling fractions of petroleum.

Read and **Williams** [2] have shown the presence of aromatic hydrocarbons in Papuan natural petroleum, which is said to be related to Borneo petroleum. The specific gravity at 22° C. (71.6° F.) is 0.7965. Besides paraffin and other saturated hydrocarbons, appreciable amounts of aromatic hydrocarbons occur. A "straight run" cut to 170° C. (338° F.) (without column) measured 10.8 per cent. From this fraction, a distillate to 120° C. (248° F.) (through a fractionating column) was obtained, which contained about 10 per cent aromatic hydrocarbons, principally benzene and toluene. The total per cent of aromatics in the crude oil is about 4; 2.4 per cent comes off in the above mentioned 120° C. (248° F.) distillate. No estimate of the amount of this oil available is given.

The Decomposition of Petroleum Oils to Yield Benzol and other Aromatic Products. — It has been said [3] that persons unfamiliar with earlier features of the production of kerosene and of oil gas are apt to think that the cracking of oil is a purely modern development, whereas the recent efforts to develop cracking processes are directed merely to effecting such modifications as are necessary to furnish a predominance of aliphatic spirit in the resultant product. For many years past the superintendent of carbureted water gas installations has known that he can produce, at will, gas and tar saturated with aromatic hydrocarbons which can be recovered and fractionated to commercial grades of benzol, etc. At the outset of the war, gas chemists pointed to the cracking of petroleum oil in existing or specially modified gas plants as the most promising means of securing a large production of toluol, and it is now only a question of price whether toluol so produced can hold its own in the market against the by-product toluol of the coal gas and coke oven industries. Egloff has recently drawn attention to the possibilities of utilizing the car-

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[1] See J. S. C. I. 1914, 852.

[2] Chem. Abs. 1919, 2126; Chem. Eng. Mining Rev. II, 259 (1919).

[3] Butterfield, Reports of the Soc. Chem. Ind. 1917, II, 78.

bureted water gas plants in operation in the United States for the production of toluol by the cracking of solvent naphtha in the presence of water gas.[1] The cracking of oil for the production of aliphatic motor spirit, however, is a somewhat more difficult proposition than that of the manufacture, by the cracking of heavy grades of petroleum, of either kerosene or benzols. It is comparatively easy to produce by cracking a good yield of "spirit" having the required range of distillation, vapor pressure, etc., but commonly such spirit contains a large proportion of relatively unstable hydrocarbon compounds, with the result that on keeping, it undergoes changes which cause gumminess and darkening of color. Methods of refining in use for petroleum distillates, if applied to such cracked crude spirit, are very wasteful and expensive owing to the ease with which a large proportion of the compounds of the spirit are attacked and generally leave a product which is still unstable and malodorous. Nevertheless skillful control of the cracking process is claimed to overcome most of the difficulty.

V. B. Lewes[2] reports that Thorpe and Young, in 1871, concluded that simultaneous formation of olefins and saturated hydrocarbons occurs by loosening of affinities of certain methane groups in heavy paraffin molecules and their recombination to form unsaturated hydrocarbons. Lewes suggests that the residuum from distillation of light cracked fractions contains naphthenes and can yield more naphthenes by cracking, but might be found to be used more profitably for the production of aromatic hydrocarbons. During the high demand for benzene in 1885 excellent results were obtained by many investigators in producing aromatic hydrocarbons from petroleum residues. It is said that residues left in the production of motor spirit crack under slight pressure at 800° to 900° C. (1472°–1652° F.) through naphthenes into aromatic hydrocarbons, producing also about 80 cubic feet gas per gallon residue treated.

E. W. Smith[3] observes that "it has long been known that various oils, specially those in crude petroleums, when subjected to the right conditions of temperature and pressure, break down or polymerize and yield a certain proportion of benzene and its homologues, the amount of which varies with the composition of the oil."

"Rhead points out that the mode of formation of benzene, etc., during the cracking of petroleum oils is parallel to that of its formation

[1] J. Ind. Eng. Chem. 1918 (10), 8; J. S. C. I. 1918, 116A.
[2] Chem. Abs. 1915, 1244; J. Gas Lighting, 1915 (129), 455; Gas World, 1915 (62), 186.
[3] Reports of Soc. Chem. Ind. 1917, vol. II, 65.

from the cracking of primary decomposition products of coal. These latter contain many compounds found in petroleums, such as naphthenes, paraffin hydrocarbons, olefins, etc., and since it is far easier to separate petroleum into simple groups of compounds than is the case with coal, a systematic study of the thermal decomposition products of petroleum oil fractions should throw much valuable light on the mechanism of coal carbonization.

" In Russia it has long been the practice to crack petroleum oils to obtain benzene and other aromatic compounds for the dye and explosive industries, the shortage of coalfields having made such an industry of vital economic importance. Moreover, Russian petroleums, being rich in naphthenes, lend themselves admirably to aromatic formation. There is little doubt that this industry, founded by the Russian chemists, led by Nikiforoff, has received a great impetus from the needs of the war.

"The first systematic work in the modern era, on producing aromatic hydrocarbons from petroleum, was carried out by **Rittman**,[1] but the large-scale installation put down at Pittsburgh as a result of his experiments has been unable to compete with other sources of benzol and toluol owing to the small yield and poor quality of the products.

"The manufacture of carbureted water gas is essentially an oil-cracking process, and the evidence so far available goes to show that a good quality benzol and toluol can be obtained by washing the gas from this process. In the early days of the war, this source was unjustly ignored, owing to the lack of a good test for the benzol content of a gas. The shortage of gas oil supplies has considerably handicapped this source in England, but it affords vast possibilities in America, the home of carbureted water gas plants."

Some tests made at the Birmingham Gas Works showed that, of the oil cracked in this process, 3 27 per cent appeared as benzol and about 2 per cent as toluol, and the products were not seriously contaminated with paraffin hydrocarbons.

Egloff [2] experimenting with a Lowe carbureted water gas plant, obtained per thousand cubic feet of gas, 0.07 gallon of benzol, 0.06 gallon of toluol and 0.01 gallon of xylol. On this basis he estimates that the carbureted water gas manufactured in America, if washed, would yield annually 8,689,000 gallons of benzol, 7,448,000 gallons of toluol, and 1,241,300 gallons of xylol.

[1] J. Ind. Eng. Chem. 1915, 7, 945; J. S. C. I. 1914, 626; 1915, 1199.
[2] Gas J. 1917, 138, 463.

Early Efforts to Obtain Aromatic Hydrocarbons from Petroleum.[1] - - As early as 1877, according to **Veith,**[2] **Letny** [3] obtained a patent for producing aromatic hydrocarbons from petroleum. **Liebermann** and **Burg,**[4] **Salzmann** and **Wichelhaus,**[5] and **Lissenko** [6] investigated the obtaining of aromatic hydrocarbons from petroleum residues at high temperatures.[7]

The presence of benzene and its homologues in crude petroleum was established at an early date. Prior to 1880 **La Rue** and **Miller** had obtained evidence of their presence in a number of crude oils.[8] Benzene has been found in Galician distillates by **Pawlewski,**[9] **Lachowicz,**[10] and others; in Baku crude oil by **Markownikoff,**[11] in crude oil from Tiflis by **Beilstein** and **Kurbatoff**; in Rangoon oil by **La Rue** and **Miller,** in Roumanian oil by **Poui,**[12] and in Canadian crude by **Schorlemmer.** Toluene was also found in the same oils by the same investigators. The proportions of these aromatics in crude oils are, however, only fractions of a per cent. For example, **Pawlewski** reports having found 0.4 per cent in Galician oil. The lower aromatic hydrocarbons, benzene and toluene, have been proven, it is said, to be almost entirely absent from American crude oils, although appreciable amounts

[1] Rittman, Dutton and Dean, manufacture of gasoline and benzene-toluene, Bureau of Mines, Bulletin 114 (1916), pp 25-29.

[2] Gewinnung aromatischer Korper aus den Ruckstanden: (Bolley and Wiedemann, Handbuch der chemischen Technologie: Erdol) 1862, p. 435; see also **Letny, Alexander,** Ueber die Einwirkung hoher Temperatur auf Petroleum, Braunkohlentheer und andere ahnliche Stoffe: Dingl. poly. Jour, Bd. 229, 1878, pp 353-365.

[3] Ueber die Zersetzung des Petroleums und des Braunkohlentheers durch Ueberhitzen. Ber Deut chem Gesell, Jahrg. 11, 1878, pp. 1210-1212; Decomposition of petroleum and lignite tar by superheating: Chem. News, vol. 38, 1878, p. 211

[4] Ueber die Zersetzung des Braunkohlentheerols in der Gluhhitze. Ber. Deut chem Gesell, Jahrg 11, 1878, pp. 723-726

[5] Ueber die Herstellung von Benzol aus Braunkohlentheerol: Ber. Deut. chem. Gesell, Jahrg 11, 1878, pp 802, 1431-1434.

[6] Zersetzung des Erdoles beim Erhitzen: Dingl. poly. Jour., Bd. 266, 1887, p 226

[7] On formation of benzene when petroleum is passed through a hot tube: Handbuch der organ Chemie, Auflag 3, Bd, 2, 1896, p. 22.

[8] Petroleum: Encyc. of Chemistry, Lippincott, 1880.

[9] Ueber das Vorkommen des Paraxylols im galizischen Petroleum: Ber. Deut. chem. Gesell., Jahrg. 18, 1885, pp. 1915, 1916.

[10] Ueber die Bestandtheile des galizischen Petroleums: Liebig's Annalen, Bd. 220, 1883, pp. 188-206.

[11] Zur Konstitution der Kohlenwasserstoffe C_nH_{2n} des kaukasischen Petroleums: Ber Deut. chem. Gesell., Jahrg. 20, Bd. 2, 1887, pp. 1850-1853.

[12] Recherches sur la composition chimique des pétroles roumains: Ann. Sci. Univ., t. 2, 1903, pp. 65-80.

of aromatic hydrocarbons of higher molecular weight are present, particularly in oils of asphaltic base.

The existence of heavier aromatics in a natural state in certain oils, particularly Russian, Roumanian, Californian, and Japanese oils, has led a number of experimenters to attempt to devise methods whereby the yields of hydrocarbons of this series can be greatly increased from such oils. Probably the most work in this field has been done with Russian and Roumanian oils, because of the peculiarly favorable nature of these oils by reason of their content of hydrocarbons of the naphthene type. It is well known that hexahydrobenzene, for example, will readily split off six hydrogen atoms and leave benzene.

Processes Patented for Production of Aromatic Hydrocarbons from Petroleum.[1] — The method devised by **Letny**[2] involved the passage of petroleum residues obtained from Baku crudes through a highly heated, horizontal retort, 7 feet long and 1 inch in diameter, filled with wood charcoal. The residues were allowed to flow through the tubes, which were heated to approximately 700° to 800° C., the vapors coming from the tubes passing to a condenser. The claim was made that 50 to 60 per cent of gas and 40 to 50 per cent of tar was obtained. The tar, on distillation, gave some 17 per cent benzol, 0.4 per cent anthracene, and 7 per cent naphthalene. The oil was fed in slowly, as Letny considered it essential that a comparatively great heating surface be exposed.

Armstrong and **Miller**[3] reported that their experiments had shown that the liquid formed during the decomposition of petroleum gases contained a mixture of hydrocarbons of the $C_{2n}H_{2n-2}$ series. The liquid was rich in benzene and toluene and showed a trace of the higher aromatic compounds. They advanced the theory that the aromatic hydrocarbons are products in direct line with the paraffins, and are not built up from the acetylene series. As previously pointed out, aromatic hydrocarbons have been found to exist in Russian and Roumanian oils; also considerable percentages of naphthene hydrocarbons which are similar in structure to the benzene hydrocarbons. These naphthenes were contained more largely in the residuum than in the crude

[1] Recherches sur la composition chimique des pétroles roumains: Ann. Sci. Univ., t. 2, 1903, p. 26.

[2] Ueber die Zersetzung des Petroleums und des Braunkohlentheers durch Ueberhitzen: Ber. Deut. chem. Gesell. Jahrg. 11, 1878, pp. 1210–1212; Decomposition of petroleum and lignite tar by superheating: Chem. News, vol. 38, 1878, p. 211.

[3] On the decomposition and genesis of hydrocarbons at high temperatures; The products of manufacture of gas from petroleum, Chem. News, vol. 51, June 26, 1885, pp. 307–309.

oil, and as a result most of the early investigators worked with the residual products.

In 1889 **Intschik** [1] patented a process for the manufacture of benzol and toluol, in which Russian petroleum residues are dropped into a highly heated vertical chamber where the oil is volatilized and the vapors decomposed. The fixed gases and vapors are drawn off and fractionally condensed. During the early eighties when the demand for benzol was high and the supply insufficient to meet the needs of the market, **Nobel Brothers, Liebermann, Burg,** [2] **Salzmann** and **Wichelhaus** [3] among others, investigated the possibilities of obtaining aromatic hydrocarbons from petroleum residues and are reported to have obtained excellent results. **Liebermann** [4] reported in 1888 that the Nobel brothers were erecting a factory in the Baku field for the purpose of manufacturing aromatic hydrocarbons from petroleum residues.

Hlawaty [5] describes a process for making benzol, toluol, xylol, cumol, naphthalene and anthracene from petroleum, residue from petroleum refineries, coal tar, coaltar oil, shaletar oil, brown coal tar, brown coal tar oil, paraffin, ceresine and vaseline, ozokerite and natural illuminating gas. Any one or any mixture of the liquid or solid hydrocarbons mentioned is put into a still, b (Fig. 203), communicating above with a closed retort, c, provided with pressure gauge, and communicating with a system of pipes and a condenser. The still b is heated quickly by means of a furnace a in such a manner that a pressure of $\frac{1}{4}$ to 1 atmosphere above the ordinary atmospheric pressure is maintained. The vapors produced are led through the pipe system, in which the less volatile products gradually condense and afterwards flow through red hot pipes d^1 while the more volatile products are carried directly to the main condenser, f.

By passing through the red hot pipes the condensed, less volatile products are partly rendered into more volatile ones which also pass to the main condenser, f, where they are mixed with the volatile products. The condensed liquid is found to consist mostly of benzol, toluol, xylol and cumol. Before entering the main condenser all the vapors are subjected to cooling and all the less volatile products are separated in order to be carried back to the retort.

[1] Russian Patent issued in 1889.

[2] Ueber die Zersetzung des Braunkohlentheerols in der Glühhitze: Ber. Deut chem. Gesell , Jahrg. 11, 1878, pp. 723–726.

[3] Ueber die Herstellung von Benzol aus Braunkohlentheerol: Ber. Deut. chem. Gesell., Jahrg. 11, 1878, pp. 802, 1431–1434.

[4] Neue Gewinnungsmethode von Benzol, Naphthalin, und Anthracen: Dingl Poly. Jour , Bd. 246, 1882, pp 429–432.

[5] British Patent 2242, Feb. 11, 1890, German Patent 51,553, Aug. 11, 1888.
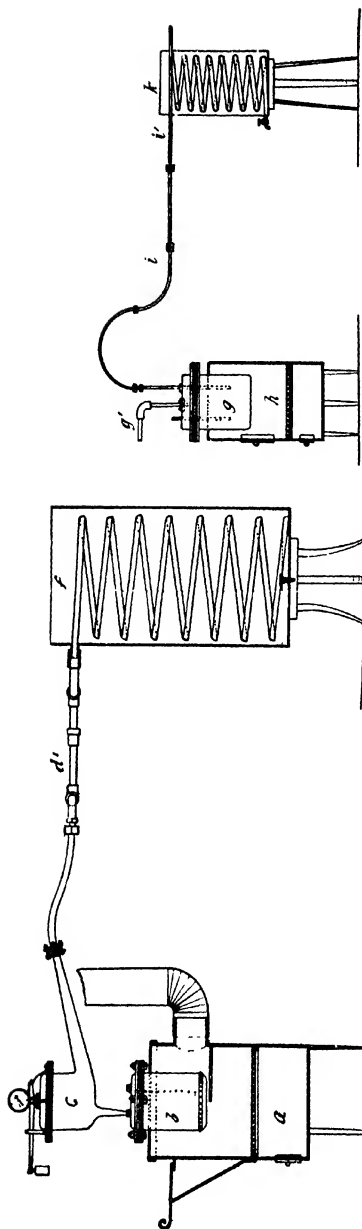
Fig. 203. — Hlawaty's process.

By this method the apparatus may be worked continuously. For this purpose it is only needful to feed the retort gradually with tar or other material to be treated. But it is necessary to interrupt the operation from time to time in order to withdraw coke. The uncondensed gases which escape from the condenser are led through red hot pipes filled with pieces of coke or pumice stone and they thus also become converted into benzol, toluol, xylol and cumol and are collected in the condenser. A separate apparatus for this purpose is not shown.

Natural illuminating gas treated in the same manner is said to yield similar products.

From the condensed liquid collecting in the condenser the benzol and other aromatic products are separated and to the residual liquid, which consists of other hydrocarbons, is added about 10 to 20 per cent, of pulverized cellulose in the form of moss, sawdust, dry, rotten wood, peat, broken coal, hay, straw or the like together with some caustic alkali. The whole is enclosed in a retort g, which is heated by a furnace h, and superheated steam at about

750° F. (400° C.) enters it by the pipe g.[1] In this manner a decided separation of the carbonaceous compounds is said to be effected. The vapors thus evolved are passed through pipes i, heated red hot. and filled with small pieces of coke or iron filings and communicating with a condenser k in which the benzol, toluol, xylol and cumol are collected. In the liquid so obtained the naphthalene and anthracene are contained ·in a dissolved condition. Instead of the steam at 750° F. (400° C.) it is advantageous to use vapors of acetic acid or of ethyl- or methyl alcohol. About 40 per cent of the liquid is stated to be converted into aromatic compounds of the kind named. **Dvorkovitz** [1] in 1892 proposed to decompose steam passed into a gasifier in which the liquid hydrocarbon is vaporized. The water gas is there carbureted and passed into a condensing chamber where the benzol, toluol, and other aromatic compounds are separated. Dvorkovitz[2] states also that the liquid hydrocarbon flows through a series of retorts in which the liquid is progressively subjected to temperatures ranging from 300° to 1000° C. (540°-1832° F.) The retorts, which are wide but shallow, are inversely inclined so that the lower end of each retort communicates with the upper end of the retort below it. The vapors from the lower retort are then passed to a condenser.

Nikiforoff [3] has developed a process for benzol-toluol manufacture involving two-stage decomposition under varying conditions. The crude oil is fed into a series of decomposition retorts, the course of the liquid being obstructed by baffle plates so as to prolong the action of the heat. A temperature of 500° to 525° C. (932°-977° F.) is maintained without pressure. The vapors pass through these retorts to a separating tank maintained at a temperature of 200° to 250° C., (392°-482° F.) where the heavier products are condensed. The more volatile products (products boiling at less than 200° C.), which remain uncondensed at that temperature, are then conducted to a separate retort where they are subjected to a temperature of 900° to 1000° C. (1652°-1832° F.) and to a pressure of about 2 atmospheres (30 pounds per square inch). (See Fig. 204.)

Nikiforoff states that in previous processes for decomposing petroleum, the entire bulk of raw material was subjected to a decom-

[1] British Patent 21,647, Nov. 26, 1892; also, **Dvorkovitz, Paul,** The distillation, cracking, and gasification of petroleum hydrocarbons: Petroleum Rev. vol. 17, Sept 28, 1907, pp 176–179; Gasification of coal and liquid hydrocarbons: Jour. Soc. Chem Ind. vol. 12, May 31, 1893, pp. 403–412.

[2] British Patent 23,671, Dec. 5, 1894.

[3] Russian Patent 290, Dec. 31, 1894; German Patent 85, Mar. 12, 1895; French Patent 315,428, Oct. 29, 1901; British Patent 10,957, Aug. 27, 1886; U. S. Patent 755,309, Mar. 22, 1904.

posing or thermolytic operation. This was the reason, he states, why earlier investigators used packings of various kinds in the retorts, such as coal, coke, iron, pumice-stone, etc. Nikiforoff, however, takes a selected distillate or condensate of crude petroleum, for cracking purposes.

Crude petroleum is passed through a retort containing staggered baffles and subjected to a temperature of about 500° C. (932° F.). This operation produces gas, residuum, coke, waste, and liquid distillate.

By fractional condensation, a fraction boiling at about 200°–250° C. (392°–482° F.) is obtained and this is selected for the high temperature
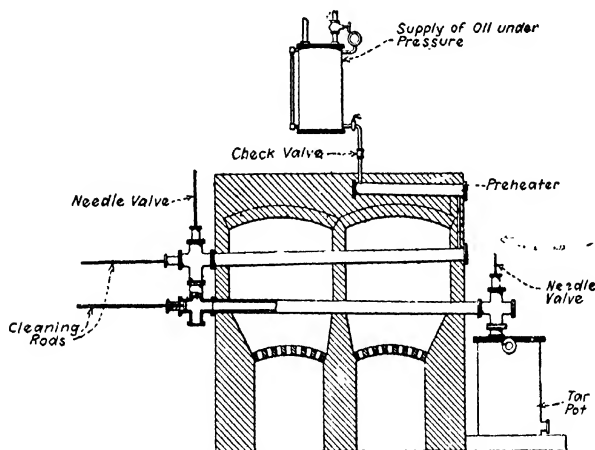
Fig. 204. — Apparatus used by Nikiforoff.

cracking process. It will be noted that the fraction he selects corresponds to a burning oil (kerosene). If a " cyclic " petroleum is operated on [for example, Balakhani (Caucasian) petroleum] a small amount of aromatic formation is said to take place in this preliminary coking operation.

The next step consists in passing this fraction through a tubular retort under pressure at a very high temperature [900°–1000° C. (1652°–1832° F.)], in the apparatus shown in Fig. 204. The selected fraction, contained in a supply tank under gas pressure passes to a preheater where it is completely vaporized and then to the decomposing retorts. Thus, as in the more recent Rittman method, the process is a strictly single phase gas process.

There is no catalytic or contact material in the retorts. Admission to and egress of the vapors from the retort is controlled by needle valves.

Cleaning rods acting on the principle of the military " ram rod " pass through stuffing boxes. Condensation does not take place under pressure. When operating on a suitable fraction of Russian oil, the pressure in the retort is only 15 pounds. The vapors pass through a tar pot, are scrubbed by heavy oil, heated to 200° to 225° C. (392°–437° F.) and finally condensed.

A few years-later Nikiforoff [1] proposed to obtain aromatic hydrocarbons by coking naphtha in a metallic retort provided with troughs along which the naphtha flows, the hydrocarbon vapors given off below 200° C. (392° F.) to be used in carbureting water gas. Air is blown through heated coke or anthracite to obtain a generator gas. Superheated steam is blown into the generator to obtain water gas. The water gas is then carbureted with the decomposition products of the naphtha. The heated water gas and hydrocarbon vapors are placed under a pressure of not less than 1 atmosphere (15 pounds per square inch). The gas and vapors are passed through a washing apparatus, where the water and heavier hydrocarbons are collected, and the gas and vaporous hydrocarbons boiling under 200° C. pass on to a condenser, which separates the liquid aromatic products and allows the gas to pass on to a collector.

In 1897, **Pamfilow** [2] obtained aromatic bodies by a process [3] involving the passage of petroleum residues through a preheater into a vaporizer, and then into a coil of many turns and great length, where the vapors are exposed to gradually increasing temperatures. He produces, it is stated, a tar, consisting almost exclusively of aromatic hydrocarbons, which upon distillation gives 15 per cent benzol, 1 per cent naphthalene, and 0.5 per cent anthracene on the basis of the original oil.

Zelinsky [4] and **Ogloblin** [5] report the obtaining of excellent results by Nikiforoff's process. The former, however, employed the method only on a small scale, treating several liters of petroleum a day. They report having been able to obtain a fraction boiling between 75° and 180° C., (167°–356° F.) which represented 14.1 per cent of the original oil, and contained 58 per cent of benzol and 28 per cent of toluol.

[1] British Patent 17,450, July 30, 1907.

[2] Gewinnung von Leuchtgas und aromatischen Kohlenwasserstoffen aus Erdol: Chem. Ztg. Jahrg. 21, Bd. 2, 1897, p. 1069.

[3] Russian Patent 322, Sept. 13, 1897.

[4] Vortrag uber die Darstellung aromatischer Kohlenwasserstoffe aus dem Erdol (Preparation of aromatic hydrocarbons from petroleum)· Chem. Ztg., Jahrg. 26, Bd. 1, 1902, p. 68; Jour. Soc. Chem. Ind 1902, 166.

[5] Die Darstellung von Benzol und seinen Homologen aus russischem Naphta nach Verfahren von A. N. Nikiforoff: Chem. Central-Blatt., Jahrg. 75, Bd. 2: 1904, p. 830.

Holcgreber,[1] passes petroleum in the form of vapor, together with an excess of pure hydrogen, through pipes filled with catalytic agents, such as iron, copper, nickel, or cobalt. The catalytic agents are used alone or mixed with an inert material such as asbestos. The tubes are kept at a temperature of 180° to 300° C. (356°–572° F.)

Another more recent proposal along somewhat different lines is that of **Starke**[2] for the production of benzene and its homologues from petroleums, particularly Japanese and California petroleums. The petroleum distillate containing the benzene and its homologues is mixed with concentrated sulphuric acid, which is heated and agitated until the evolution of sulphur dioxide has ceased. The mass is then allowed to settle until the sulphonic acids have separated from the petroleum, and the benzene is then recovered by ordinary distillation.

Other processes of the same type as that last mentioned are those developed by the **Disconto Gesellschaft**[3] in Berlin and by **Tammann.**[4]

Testelin and **Renard**[5] and **Meffert**[6] use a mixture of superheated steam and oil, which is very highly heated, to produce aromatic hydrocarbons. Testelin and Renard pass the mixture over a layer of red hot clay, whereas Meffert heats the mixture in refractory retorts to a temperature of 1200° to 1400° C. (2192°–2552° F.) Neither process employs pressure. **Testelin** and **Renard** claim that the use of pressure is prejudicial.

Selinsky[7] states that the carbonaceous deposit which is formed in considerable quantities when petroleum is cracked in iron retorts contains about 70 per cent of carbon and 30 per cent of iron When decomposed with hydrochloric acid it yields a mixture of combustible gases containing 85 per cent of hydrogen, 12 per cent of methane and 2 2 per cent of olefins The best yields of benzene and toluene are said to be obtained when petroleum is cracked in tubes filled with alumina and titanium oxide, which act as catalysts.

The **Société Lyonnaise des Eaux et de l'Éclairage**[8] cracks tars and mineral oils for the production of benzol, gasoline, etc., by introducing them into a continuous circulation of anthracene oils or vapors, or other high-boiling oils or vapors. The vapors resulting from the reaction are passed into rectifying columns; the gases and vapors

[1] British Patent 17,272, July 28, 1913.

[2] U. S. Patent 913,780, Mar. 2, 1909; See also U. S. Patent 1,109,187, Sept. 1, 1914.

[3] German Patent 216,459, May 23, 1908.

[4] German Patent 95,579, Mar. 3, 1897.

[5] German Patent 268,176, Aug. 11, 1908.

[6] German Patent 99,254, Mar. 13, 1897.

[7] J. S. C. I. 1916, 957; J. Russ. Phys.-Chim. Obschtestwa, 1915, 9. Chem. Zeit. 1916, 40, Rep. 285.

[8] Chem. Abs. 1917, 95; British Patent 9729, July 3, 1915.

issuing from the top of the column pass to condensers and washers; the liquids from the base of the column are retained for further treatment. The anthracene vapors may be preliminarily converted by treatment in the presence of steam, into anthraquinones which are more easily transformed into benzol, toluol and light spirit.

Oppenheimer [1] utilizes water gas tar as a source of fuel for internal combustion engines. After dehydration with lime, it is distilled until the residue is pitch. The crude distillate is then treated with sulphuric acid and strong soda solution and redistilled. The first runnings are said to amount to 10–50 per cent of the crude distillate and to have a specific gravity of 0.820 0.900. It is free or almost free from sulphur and phenols, its boiling temperature is approximately between 100° and 210° C. (212°–464° F.) and it contains toluene, ortho-, meta-, and paraxylene, mesitylene and a trace of naphthalene; but the bulk of it consists of hydrocarbons, the chemical nature of which has not, it is said, yet been elucidated. In comparison with other petroleum spirits it is claimed to possess the advantage that its flash-point is considerably higher, being about 79° F. The product is claimed to be suitable for the manufacture of varnish and coloring-matters, also in the textile trades — for instance, for cleaning wool, as a solvent for india-rubber, gum, resin, and other materials and as a combustible liquid for working internal-combustion engines.

Greer [2] recovers and utilizes the light oil which condenses in the coolers, receivers, pipes and purifiers of gas works when oil is used for carbureting or generating purposes. He then distills the recovered light oil and uses it as a solvent as well as fuel for motors.

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[3] Courtesy United Gas Improvement Co.

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CHAPTER XXV

ALCOHOL AS MOTOR FUEL

To alcohol we may look for substantial additions to the world's supply of motor fuel. As one official report expresses the situation, the outstanding and fundamental attraction of alcohol in substitution for fuel obtained from coal or oil deposits resides in the fact that alcohol is derived from the vegetable kingdom, from supplies of raw material which are being continuously renewed and are susceptible of great expansion without encroachment upon food supplies. Fermentable material from which alcohol may be obtained is available everywhere, but food requirements demand that alcohol for fuel purposes in the main be restricted to inedible waste or by-products. The use of potatoes, corn, cereals and other products of agriculture which are yielded at the expense of much labor and utilization of arable soil, as a source of motor spirit is not likely to be countenanced indefinitely. The shrubs or other vegetation of waste lands, the by-products of sugar refineries, the garbage of large cities, the waste sulphite cellulose liquor of paper mills, low grade starchy materials and wood, peat or cellulose itself afford sources of alcohol. From sawdust, alcohol of good quality may be produced. The transportation requirements of the world are so great that to cope with the approaching dearth of gasoline, now forecast, raw materials in substitution for it should be accessible in great quantities. From now on the globe will be minutely searched not only for petroleum and coal but for areas productive of raw material for the manufacture of alcohol.

A recent commercial development is that of converting the ethylene of coke-oven gas into ethyl alcohol. In the waste gases of the petroleum refinery reside a source of a considerable amount of alcohol, especially propyl and higher alcohols. The unsaturated components of these gases are capable of conversion, with good yields into these alcohols. One of the authors of this volume for many years past has extensively investigated this phase of the fuel situation and recognizes possibilities of a substantial development in the gasoline refinery along such lines.

By itself, alcohol is not a fuel well adapted for present types of engines. Unfortunately alcohol has a very slow rate of combustion. Compression far higher than can be employed with gasoline is necessary

to get from alcohol the most efficient utilization of its energy value. But alcohol is a good mixer and may be associated with other fuels to advantage. Besides alcohol, the present or prospective basic sources of volatile liquid fuel are probably limited to gasoline (and kerosene), benzol, and shale spirit. Benzol and alcohol are perfectly miscible and the addition of alcohol to benzol overcomes the objection of the freezing of the latter in cold weather. Shale spirit has gumming or resinifying tendencies which may be ameliorated by alcohol. The lightest grades of gasoline mix with alcohol, but with the heavier grades and particularly with kerosene separation occurs. This however may be corrected by the addition of a mutually miscible solvent such as benzol. In the past much study has been given to the blending of gasolines from different sources in order to improve the fuel qualities and to cheapen the cost of production, and the future offers many possibilities in the way of blending alcohol with hydrocarbons from different sources to yield fuels approximating in closest degree to the requirements of an ideal fuel. Volatility and ease of starting, maximum compressibility with freedom from tendency toward preignition, uniform explosibility, rapidity of combustion, avoidance of carbon deposits or injury to cylinders embrace some of the points to be considered.

Owing to the slow rate of combustion of alcohol, such use as has been made of it for the purpose has been mainly with slow-speed, stationary engines. Efforts to increase the velocity of explosion by compounding or blending as above have yielded successful results. Some interesting work has been carried out by charging alcohol with acetylene and the gases of a cracking plant, e.g. ethylene, butylene, propane and butane, which may offer an important clue to the improvement of alcohol from a fuel standpoint.

Alcohol is a cleaner fuel than gasoline, its use being marked by absence of smoke and the disagreeable odors arising when gasoline is burned with an improper air supply. The hazards involved in the storage and handling of alcohol are less than in the case of gasoline. Burning alcohol is extinguishable by water.

From the foregoing it will be concluded that although the difference in price between gasoline and alcohol now is an obstacle to the extensive use of the latter, such a differential probably will not long prevail, and the authors venture the suggestion to manufacturers of motor cars, trucks and tractors and to others interested in the future welfare of the self-propelled vehicle that the problem of adaptation of alcohol and alcohol-containing fuels to such usages is a timely one.

The fundamental drawback as regards alcohol for fuel purposes is that the raw materials which can be made to produce alcohol are so

widely scattered that, although there is an annual *potential* supply
of many billions of gallons, only a minute fraction of this quantity can
be commercially obtained and this is chiefly supplied by molasses from
the West Indies and other localities favorable to the growth of sugar
cane.

White [1] states that while it has always been the aim of designers to
make the gasoline motor as flexible as the steam engine, the narrow
range within which a charge of gasoline and air can vary in composition
and yet remain explosive has always prevented any regulation of the
power by the manipulation of the mixture. In the case of alcohol and
air, the variation of the proportions compatible with perfect com-
bustion is 4 times as great and it has been determined by experiment,
it is stated, that the specific power of the working stroke of an alcohol
engine can be reduced to 25 per cent of the maximum by the operation
of an auxiliary air throttle. This means that the adoption of alcohol
in automobile practice would tend toward fewer cylinders and simpler
gears. Rough limits within which mixtures of air with alcohol and
with gasoline are, respectively, explosive are alcohol 4 to 14 per cent
and gasoline 2 to 5 per cent.

When one pound of absolute alcohol and one pound of gasoline
(hexane) are completely burned, each in a suitable motor, the follow-
ing numerical relations are independent, it is said, of the type of motor
used.

	Alcohol	Gasoline
Minimum sufficient amount of air	9 pounds.	15.3 pounds.
	117 cubic feet	198.9 cubic feet
	at 150° C. and	at 150° C. 760
	760 mm. pressure	millimeters.
Carbon dioxide in exhaust	{ 1.9 pounds	{ 3 pounds
	{ 15.9 cubic feet	{ 25 1 cubic feet
Nitrogen in exhaust	{ 6 9 pounds	{ 11.8 pounds
	{ 90.6 cubic feet	{ 155 cubic feet
Water condensed from exhaust	1.2 pounds	1.5 pounds

It is observed that there are 5 pounds more nitrogen in the exhaust
from 1 pound of gasoline than from 1 pound alcohol. This is as-
serted to mean an additional loss of heat in exhaust and a tendency to
cause incomplete combustion, owing to dilution, in the case of gasoline.

Preheating the mixture after the fuel is in a state of vapor is hamp-
ered because owing to the expansion, the actual weight of mixture
going in on the suction stroke is decreased so that specific power of
the motor is decreased.[2]

[1] Eng. Magazine, 1908, 876, *et seq.*   [2] *Ibid.* p. 878.

Some of the disadvantages of alcohol are as follows: [1]

1. The fuel ignites slowly compared to gasoline and, when ignited, the propagation of the flame throughout the mixture is not sufficiently rapid to be compatible with a piston velocity of over 12 feet per second, and a piston travel, which, at any rate in the case of the automobile motor, is strictly limited.

The disadvantages from this sluggish ignition and tardy inflammation are: [2]

1. Combustion, instead of being completed when compression and temperature are highest, is continuous during entire expansion, meaning that a portion of the heat units are not being utilized, from a thermodynamical standpoint, to best advantage.

2. This imperfect combustion leads (when methyl alcohol is present) to the formation of acetone, which during the expansion stroke is partly oxidized to acetic acid.

The problem of substituting alcohol for gasoline as a fuel in the high speed motor is stated to involve [3] securing of a more vigorous ignition and speedy inflammation. The use of acetylene in this respect is looked upon with favor. The acetylene molecule tends to detonate and become a center of inflammation and the whole mass is burned with a speed and vigor which is limited only by the proportion of acetylene present.

Bornn [4] referring to the report made by **Johnson** of the Hawaiian Sugar Planter's Association on the development of alcohol as motor fuel, states that during the war an alcohol motor fuel was produced in South Africa and subsequently in Hawaii which proved to be equal to the best quality of gasoline available.

As finally developed, the fuel was a mixture of alcohol, ether and pyridine. Pyridine burns to ammonia, carbon dioxide and water and was used to render the products of combustion alkaline or at least non-acid. It also acted as a denaturant.

Bornn, [5] observes that when alcohol motor fuel is substituted for gasoline the steam which results from the water naturally in the alcohol, and also formed by the combustion of the latter, aids in preventing the formation of carbon deposit.

R. M. Strong and **Lauson Stone** [6] have made a series of exhaustive tests in comparing gasoline and alcohol, using stationary Otto and Nash engines.

[1] *Ibid.* p. 879, *et seq.*   [2] *Ibid.* 880.   [3] *Ibid.* p. 88.
[4] The Evening Post Foreign Trade Review, October, 1919, Chemical Section.
[5] The Evening Post Trade Review, October, 1919, Chemical Section, p. iv.
[6] Bureau of Mines Bulletin 43, " Comparative Fuel Values of Gasoline and Denatured Alcohol in Internal Combustion Engines," 1912.

Two Otto gasoline engines and one Otto alcohol engine of the single cylinder, horizontal, 4-cycle, stationary type, rated at 15 brake horse power at a speed of 260 revolutions per minute were used. Also two Nash engines were used, one alcohol and one gasoline, both of the single cylinder, 4-cycle, stationary type, and having horse powers rated at 10 with a normal speed of 280 revolutions per minute.

It is observed, from a consideration of the standard formula for the thermal efficiency of the ideal air engine

$$E = 1 - \left[\frac{Pa}{Pb}\right]^{\frac{r-1}{r}}$$

in which E is the thermal efficiency, Pa the initial pressure (absolute), Pb the compression pressure, and r the ratio of specific heat at constant pressure to specific heat at constant volume, that with a constant specific heat of the exhaust gases, the efficiency must increase with an increase in the compression pressure, Pb.

They have plotted a series of curves for air, alcohol and gasoline (specific gravity at $60°$ F. $= 0.7122$. Heating value: high 20,581, low 19,292 B.T.U. per pound), showing the relation between *indicated thermal efficiency* (calculated from indicated horse power and low heating value of fuel and *compression pressure* (see Fig. 205)).

On the basis of the indicated thermal efficiencies and compression pressures corresponding to maximum thermal efficiencies, the value of the exponent $\dfrac{r-1}{r}$ in the above thermodynamical formula has been calculated as follows (see also Fig. 205):

$$\text{For gasoline} = 0.17$$
$$\text{For alcohol} = 0.19$$

Constant for air $= 0.29$

Hence the equations become:

For gasoline
$$E = 1 - \left(\frac{Pa}{Pb}\right)^{.17}$$

For alcohol
$$E = 1 - \left(\frac{Pa}{Pb}\right)^{.19}$$

It is stated, however, that the thermal efficiencies obtained for the different clearance ratios and corresponding degrees of compression fulfill these equations only when the maximum thermal efficiency of the engine is obtained, which requires that the engines be in the best possible running condition and operated to the best advantage. It is also stated that if the engines referred to (Otto and Nash) are operated
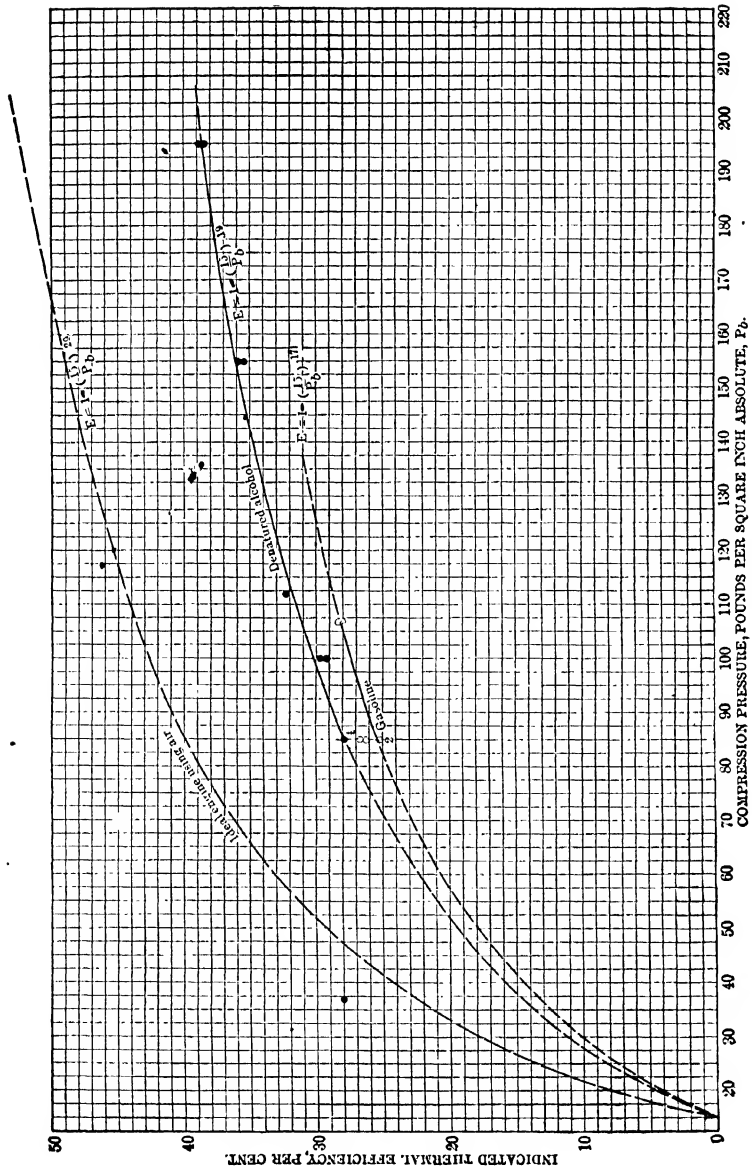
Fig. 205.

under different conditions with respect to throttling of the charge, the maximum thermal efficiencies obtained will not fulfill the same equation.[1]

In other words the calculated relationships shown above are quantitative only when the thermal efficiency of the engine is at its maximum value.

In the curve shown in Fig. 205, indicated thermal efficiency is correlated with compression pressure. The first curve shows the conditions which might be expected with the ideal engine with air as the working medium. The other two show to what degree this ideal condition has been approached with the gases obtained from the combustion of denatured alcohol and gasoline as the working medium. Strong and Stone[2] observe that denatured alcohol more nearly approaches the ideal fuel than does gasoline, for at any one compression it shows a greater efficiency. Since the denatured alcohol curve and the gasoline curve were both plotted by means of two similar formulas,

differing only in the value of the exponent $\dfrac{r-1}{r}$, this value offers a reason why denatured alcohol appears to be a more ideal fuel than gasoline. With increasing values of $\dfrac{r-1}{r}$ from 0 to 0.29 (the value for

air in the ideal air engine) it is seen that increasing efficiency approaching the ideal may be obtained. Since this exponent has been determined as 0.19 for denatured alcohol and 0.17 for gasoline, it would appear that r for the gas resulting from the combustion of denatured alcohol must be greater than that of the gases resulting from the combustion of gasoline.

It seems, then, that some explanation for the greater efficiency with which denatured alcohol may be used at a given compression may be found in the character of the exhaust gases. However, because of the changing character of the gases as combustion progresses and the consequent changes in specific heat, a study of this feature will be surrounded with many difficulties. Nevertheless future work along this line could be profitably spent, it is observed, in analysis of exhaust gases with a view to learning something of their specific heats in the hope that knowledge thus gained may enable investigators to attack the problem in the future with greater intelligence and knowledge of the principles involved.

[1] **R. M. Strong,** Bureau of Mines Bulletin 32, Deductions from Comparisons of Gasoline and Alcohol Tests on Internal Combustion Engines, 1911.

[2] *Loc. cit.*

R. M. Strong[1] summarizes and discusses the results of 2000 tests conducted by the technologic branch of the United States Geological Survey, to determine the relative economy and efficiency of gasoline as compared with alcohol, when used in stationary engines. The results are of fundamental importance since they point out the thermodynamic and practical relationship between the two fuels.

It is concluded that

1. The low heating value of completely denatured alcohol will average 10,500 British thermal units per pound, or 71,900 British thermal units per gallon.

The low heating value of 0.71 to 0.73 specific gravity gasoline will average 19,200 British thermal units per pound, or 115,800 British thermal units per gallon.

The low heating value of a pound of alcohol is approximately six tenths of the low heating value of a pound of gasoline.

A pound of gasoline requires approximately twice the weight of air for complete combustion as a pound of alcohol.

The heating value of a cubic foot of an explosive mixture of alcohol vapor and air having theoretically just sufficient air for complete combustion is approximately equal to that of a cubic foot of a similar explosive mixture of gasoline vapor and air – about 80 British thermal units per cubic foot.

2. Explosive mixtures of alcohol vapor and air can be compressed to much higher pressures in an engine cylinder without preigniting than can explosive mixtures of gasoline vapors and air. The maximum pressure of compression that can be used without causing preignition will in each case depend partly on the quality of the explosive mixture, on the design of the engine, and the speed at which it is operated.

For 10 to 15 horsepower four-cycle stationary engines of the usual type a compression pressure of about 70 pounds per square inch above atmospheric was found to be the maximum that could be used for gasoline mixtures, and about 180 pounds the maximum that could be used for alcohol mixtures without causing preignition.

The maximum compression pressure that could be used without causing preignition was in each case found to be the most advantageous from the standpoint of fuel economy.

3. When the degree of compression is in each case that best suited to the economical use of the fuel designated, some types of gasoline engines are better adapted to the service for which they are designed than similar alcohol engines and vice versa. The relative amount of fuel consumed being disregarded, this is also true when the degree of compression is that ordinarily used for gasoline mixtures, as when denatured alcohol is used in gasoline engines; but in general the alcohol engine is or can be so designed and constructed as to be equal to the gasoline engine in adaptability to service.

A gasoline engine having a compression pressure of 70 pounds but otherwise as well suited to the economical use of denatured alcohol as gasoline will, when using alcohol, have an available horsepower about 10 per cent greater than when using gasoline.

When the fuels for which they are designed are used to an equal advantage, the maximum available horsepower of an alcohol engine having a compression pressure of 180 pounds is about 30 per cent greater than that of a gasoline engine having a compression pressure of 70 pounds, but of the same size in respect to cylinder diameter, stroke, and speed.

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[1] Bureau of Mines Bulletin 32 (1911).

When denatured alcohol is used in 10 to 15 horsepower four-cycle stationary engines having a compression pressure of approximately 180 pounds and the engines are operated at their maximum loads, the pressures during explosion or combustion reach 600 to 700 pounds. Stationary gasoline engines, in which the compression pressure in some cases can be raised to 180 pounds, are not usually built heavy enough to withstand such explosion pressures for any length of time.

4. A gasoline engine having the degree of compression ordinarily used for gasoline mixtures will in general require 50 per cent more denatured alcohol than gasoline per brake horsepower per hour.

Gasoline and alcohol engines of similar construction having degrees of compression best suited to the fuel supplied will in general require equal volumes of gasoline and denatured alcohol, respectively, per brake horsepower per hour.

Gasoline engines of the usual four-cycle stationary type will ordinarily consume about a pint of gasoline per brake horsepower per hour when operated at about rated load and with a reasonably favorable adjustment of the mixture quality and time of ignition.

When carrying light loads or carrying their maximum loads, gasoline and alcohol engines governed for constant speed require a greater quantity of fuel per brake horsepower per hour than when carrying their rated loads, if rated at about 75 to 80 per cent of their maximum loads; but unless the mixture quality and time of ignition are adjusted to suit each change of load, the rate of consumption per brake horsepower per hour will in general be least at maximum load and will increase with decrease in load.

When any of the usual methods of governing are used to control the speed of gasoline or alcohol engines, the rate of fuel consumption per brake horsepower per hour will ordinarily be about twice as great at one-third load as at maximum load. At the same time an excessive rate of consumption of gasoline or denatured alcohol at any given load, if due to the incorrect adjustment of the mixture quality and time of ignition only, may be as great as, but not greater than approximately twice the minimum required before it will be noticeable from outward indications.

5. The thermal efficiency of alcohol and gasoline engines will in general increase with the pressure to which the charge is compressed when ignited.

The maximum thermal efficiency of 10 to 15 horsepower four-cycle stationary engines of the usual type when operated with a minimum amount of throttling was found to increase with the compression pressure according to the formulas

$$E = 1 - \left(\frac{14.7}{P}\right)^{.17} \text{ for gasoline and } E = 1 - \left(\frac{14.7}{P}\right)^{.19} \text{ for alcohol, } \textit{where } E = \textit{the}$$

thermal efficiency based on the indicated horsepower and low heating value of the fuel and P = the indicated pressure of the charge at the end of the compression stroke in pounds per square inch absolute.

6. A high thermal efficiency and a rate of consumption of less than a pint per brake horsepower per hour, both for gasoline and for denatured alcohol, can often be obtained when the degree of compression, the load, the quality of the explosive mixture, and the time of ignition are carefully adjusted. A fair representation of the best economy values obtained, taken from the results of tests on 10 to 15 horsepower Nash and Otto stationary engines, and the corresponding thermal efficiencies are given in the following table:

Results from Tests made on 10 *to* 15 *Horsepower Nash and Otto Stationary Engines*

Fuel	Compression pressure (pounds) [1]	Fuel consumed per brake horsepower per hour		Thermal efficiency (per cent) [2]
		Pound	Gallon	
Gasoline	70	0.60	0 100	26
	90	.58	.097	28
	70	.96	.140	28
Alcohol	180	.71	.104	39
	200	.68	.099	40

7. When by means of a double carburetor gasoline and alcohol are used simultaneously in varying proportions from practically all gasoline to practically all alcohol, the most advantageous degree of compression will vary from that found to be the best for gasoline mixtures to that found to be the best for alcohol mixtures.

Tests that were made with such an adjustment of compression indicate that the total amount of fuel (gallons of gasoline + gallons of denatured alcohol) required for any given load is practically constant for the entire range of proportions from all gasoline to all denatured alcohol.

8. When water is sprayed into an explosive mixture of gasoline vapor and air as it is being taken into the cylinder of an engine and is introduced at the most advantageous location, it may in many cases be supplied in amounts up to as much water as gasoline by weight without affecting the performance of the engine, except as noted below.

The capacity or maximum available horsepower of an engine decreases with an increase in the percentage of water, by weight, present in the explosive mixture of gasoline vapor and air.

When used in an engine having a constant degree of compression, the presence of water in an explosive mixture of gasoline vapors and air in quantities equal to or less than the weight of gasoline does not increase or decrease the amount of gasoline required to carry any given percentage of the corresponding maximum available load.

The pressure to which an explosive mixture of gasoline vapor, water, and air can be compressed in an engine cylinder without preigniting increases with an increase in the percentage of water in the mixture, and can be raised to about 140 pounds when the weights of water and gasoline are equal.

That the amount of gasoline required is not affected by an increase in the compression pressure when preignition is prevented only by the introduction of

[1] Per square inch above atmosphere.

[2] Based on the indicated horsepower and the lower heating value of the fuel.

water as above stated is indicated by the results of tests made on an engine having a compression pressure of 130 pounds. These tests are limited, however, and the results are not conclusive.

9. Alcohol diluted with water in any proportion from denatured alcohol, which contains about 10 per cent of water, to mixtures containing about as much water as denatured alcohol can be used in gasoline and alcohol engines if they are properly equipped and adjusted.

When used in an engine having a constant degree of compression, the amount of pure alcohol required for any given load increases and the maximum available horsepower of the engine decreases with a diminution in the percentage of pure alcohol in the diluted alcohol supplied. The rate of increase and decrease respectively is such, however, that the use of 80 per cent alcohol instead of 90 per cent, or denatured alcohol, has but little effect on the performance of the engine; so that if 80 per cent alcohol can be had for 15 per cent less cost than 90 per cent alcohol and could be sold without tax when denatured, it would be more economical to use the 80 per cent alcohol.

When an engine is supplied with diluted alcohol, the compression pressure that can be used without causing preignition increases with an increase in the percentage of water by weight in the mixture, but no tests were made to determine the effect of increased compression pressure on the economy with which diluted denatured alcohol could be used.

10. The relative hazard involved in the storage and handling of gasoline and denatured alcohol is of particular importance in considering their use as fuels for marine and factory engines and engines to be placed in the basements of office buildings, in coast-defense fortifications, or in like places where a general fire would be likely to result from the accidental burning of the fuel stored or carried for immediate supply, or where the forming of explosive or inflammable mixtures of the fuel vapors and air in the immediate vicinity would be hazardous.

11. In regard to general cleanliness, such as absence of smoke and disagreeable odors, alcohol has many advantages over gasoline or kerosene as a fuel The exhaust from an alcohol engine is never clouded with a black or grayish smoke, as is the exhaust of a gasoline or kerosene engine when the combustion of the fuel is incomplete, and it is seldom, if ever, clouded with a bluish smoke when a cylinder oil of too low a fire test is used or an excessive amount supplied, as is so often the case with a gasoline engine. The odors of denatured alcohol and the exhaust gases from an alcohol engine are also not likely to be as obnoxious as the odor of gasoline and its products of combustion.

12. Very few alcohol engines are being used in the United States at the present time, and little has been done toward making them as adaptable as gasoline engines to the requirements of the various classes of service. Engines for stationary, marine, and traction service, automobiles, motor trucks, and motor railway cars designed especially to use denatured alcohol have, however, been tried with considerable success.

The price of denatured alcohol is greater than the price of gasoline, and the quantity of denatured alcohol consumed by an alcohol engine as ordinarily constructed and operated is in general relatively greater than the quantity of gasoline consumed by a gasoline engine of the same type. Considerable attention is being given to the development of processes for the manufacture of alcohol from cheap raw materials which are generally available, and it seems reasonable to expect that the price of denatured alcohol will eventually become as low as or lower than the price of gasoline, especially as the price of gasoline advances.

When used as a fuel, denatured alcohol is not always so classed as to be exempt from restrictions placed on the use of gasoline by the rules of insurance and transportation companies or city ordinances. The restrictions that are placed on the use of denatured alcohol are, however, never greater than those placed on the use of gasoline. In some places they are such that the use of an alcohol engine is permitted where the use of a gasoline engine is prohibited. For instance, alcohol motor trucks and automobiles are admitted to certain steamer piers in New York that are not usually open to gasoline machines.

Where the restrictions placed on the use of denatured alcohol are less than those placed on the use of gasoline or where safety and cleanliness are important requisites, the advantages to be gained by the use of alcohol engines in place of · gasoline engines may be such as to overbalance a considerable increase in the fuel expense, especially if the cost of fuel is but a small portion of the total expense involved, as is often the case. Denatured alcohol will, however, probably not be used for power purposes to any great extent until its price and the price of gasoline become equal and the equality of gasoline and alcohol engines in respect to adaptability to service required and quantity of fuel consumed per brake horsepower, which has been demonstrated to be possible, becomes more generally realized.

A further general development in the design and construction of engines that use kerosene, or cheaper distillates, and the crude petroleums may be reasonably expected and may delay the extensive use of denatured alcohol for some time to come, but as yet comparatively few data pertaining to this phase of the general investigation are available.

Concerning the use of alcohol as a motor fuel, **J. S. Critchley** [1] states, that in Germany, with stationary alcohol motors, efficiencies have been obtained reaching as high as 35 to 38 per cent; such results, however, can only be obtained by very high compression and by the addition of water to the fuel mixture in an amount proportional to the compression. An efficiency of 30 per cent, however, can be taken as representing the average which can be obtained with a well designed stationary alcohol motor. Even taking the efficiency of alcohol at 30 per cent and the efficiency of gasoline at 20 per cent it will be found, it is asserted, that there is a gain of at least 10 per cent in favor of gasoline by volume. It would seem, therefore, that under the best conditions a gallon of alcohol would never have the same value as a gallon of gasoline. Under normal compressions all records go to prove that the consumption of alcohol is at least 50 per cent greater than that of gasoline. It has yet to be proved that alcohol can be utilized at a high efficiency with a small high speed engine. All data we have as to efficiency have been obtained with slow running stationary motors.

The slow rate of flame propagation is claimed by some to be an advantage. No doubt it gives a somewhat smoother running engine, but it is undoubtedly at the expense of power. Alcohol is a fuel which can only be considered provided it can be utilized as cheaply as other

[1] As reported in the Motor Truck, Nov. 1913, p. 877.

fuels. It is quite evident that 90 per cent alcohol, as we know it, is not to be compared with gasoline for high speed motors. Its heat value is low, there is difficulty in starting from cold and it requires high compression if it is to be used with economy. The gasoline engine as now constructed is quite unsuitable for alcohol, and even if alcohol were available as a fuel today the price would have to be a very low one indeed to compete with other fuels. In Germany, where the question of alcohol has been thoroughly studied, this fuel is used only for slow speed stationary engines.

W. T. Rowe [1] notes that alcohol possesses many advantages over gasoline as a fuel for internal combustion engines. A greater degree of compression can be used and there is less trouble from " knocking." A mixture has been used consisting of 95 volumes of alcohol and 5 volumes of water. Methylated spirit is more economical but would be improved by using better denaturing agents. There is, of course, difficulty in starting from " all cold " with alcohol, and it is advantageous to add a little gasoline or ether. With engines specially designed for alcohol, this fuel has an advantage over gasoline, relative efficiencies of 28 and 16.5 per cent respectively being quoted. (See also J. S. C. I. 1915, 336.) Gasoline and alcohol do not mix in all proportions, but gasoline may be added, it is stated, to 95 per cent alcohol up to equal volumes. Benzol will mix with alcohol in all proportions, and in some cases a solution of naphthalene in benzol is used. With regard to the revenue restrictions it is recommended to provide a system of methylation more adapted to a motor spirit: benzol, gasoline or redistilled condensate from Pintsch gas are suggested as admirable denaturants for this purpose. The use of wheat for alcohol production renders the cost prohibitive, and the price of potatoes would require to be not higher than $5.52 per ton. A good source of alcohol is found in molasses, of which in Australia fully a third is put to no use. Wood, according to the variety, will give 16 to 20 gallons of alcohol per ton. As regards the cost of alcohol, the working expenses, apart from the restrictions of the Revenue authorities, would appear, it is stated, perhaps somewhat optimistically, to average about 10 cents per gallon.

Watson, Frost, Lloyd, Richards, Stern, Shaw and **Wilson** [2] have studied the question of carburetion, particularly when starting, and in cold weather, with fuels such as benzol, alcohol and some of the heavier brands of gasoline. The importance of this question is noted and tests have been carried out comparable with those of gasoline. (See Proc. Inst. Automob. Eng. 7, 35.)

[1] J. S. C. I. 1917, 996; Bull. No. 8, Dept. of Chem.
[2] J. Soc. Chem. Ind. 1915, 266; Inst. Automobile Eng. Dec. 1914.

Alcohol. — Experiments were made with ordinary methylated spirit in a jet carburetor, a larger jet being used than in the case of benzol and gasoline; it was also found necessary to supply additional heat to the carburetor, which was done by passing a current through a wire wound round the pipe leading from the jet to the throttle. This was not altogether sufficient, and owing to the irregular vaporization of the fuel, irregular exhaust gas measurements were obtained. The mean effective pressures obtained with alcohol were slightly higher than those obtained with either gasoline or benzol, and increased more rapidly with the strength of the mixture than in the cases of the other fuels. When using the strongest mixture, six parts of air to one of alcohol, the mean effective pressure was still increasing with the strength of the mixture, and 6 per cent carbon monoxide was found in the exhaust gases. Obviously this means that maximum power can only be attained by appreciable loss due to incomplete combustion.

Maximum thermal efficiency, as also that at complete combustion, increases slightly from gasoline to benzol and benzol to alcohol, and the temperatures attained with the three fuels do not differ much, though those with alcohol are a little lower than the others, which may account for the slightly higher thermal efficiency obtained with alcohol. Unless the vapor tension of the fuel in the cylinder is above a certain limit it is impossible to obtain an explosive mixture. This difficulty may be easily overcome in the case of gasoline as owing to the presence of highly volatile constituents it is possible to flood the cylinder and so obtain an explosive mixture. With benzol and alcohol no such volatile bodies are present, and consequently starting difficulties are encountered in cold weather. Experiments with different liquid fuels were made in a closed vessel, and it was found that with a very volatile brand of gasoline an explosive mixture could be obtained at 0° C. and a pressure of 40 pounds per square inch. Air saturated with benzol vapor below 1° C. (33.8° F.) at atmospheric pressure is incombustible, and at temperatures below 20° C. (68° F.) air saturated with alcohol vapor is incombustible even at atmospheric pressure. When used in the engine the heat generated by the compression produced by starting the engine by hand is sufficient to vaporize the fuel, except, perhaps, in the case of alcohol, or, when the fuel is already vaporized, to keep it in the form of vapor during the compression.

M. B. Blackler [1] observes that a peculiar property of hydrocarbons obtained by cracking processes, which would influence the fuel question, is that these spirits, unlike " straight " gasoline, mix with alcohol.

[1] In a discussion of "The Pyrogenesis of Hydrocarbons" by **Lomax, Dunstan** and **Thole,** Journ. Institution of Petroleum Technologists, 1916 [3], 36–120.

It had been previously determined that alcohol mixed with a certain quantity of benzol was an excellent fuel for a gasoline engine and Blackler feels confident that in the future, when the supply of gasoline becomes insufficient for the world's demand, cracked spirit obtained from heavy hydrocarbons will be mixed with alcohol in proportions up to 50 per cent, and used as fuel for high-speed internal-combustion engines. An interesting point is the boiling-point of such a mixture. When purified cracked spirit, boiling from 35° to 220° C. (95°–428° F.), was mixed with an equal quantity of alcohol, 90 per cent of the mixture boiled below 100° C. (212° F.)

Hall[1] cracks heavy hydrocarbon oil at about 600° C. (1112° F.) until about 25 per cent is converted into gas, composed mainly of hydrocarbons of the ethylene series. The gases are mixed with alcohol vapor and the mixture is condensed under pressure.

Hall observes that it has been proposed in the past to adapt alcohol as a fuel for use in motor cars and internal combustion engines generally by mixing with it benzol which, when used in such proportions as 33 to 50 per cent, makes an excellent motor fuel when quick running is not essential; but even such mixtures as these show difficulty in starting from cold if the temperature is low, while the cost of the benzol is but little below that of gasoline. It has also been proposed to dissolve acetylene in alcohol in order to give the necessary ease in starting the motor and to accelerate the running, but when sufficient acetylene is added for this purpose carbon is liable to deposit in the cylinder and high compression is accompanied by pre-ignition.

It has been found that heavy hydrocarbon gases are dissolved by alcohol in large quantities, for instance one volume of alcohol will dissolve from 12 to 15 volumes of butylene at ordinary pressures. Ethylene and also saturated gases, propane, butane and ethane are soluble in alcohol. Such a solution produces a fuel having the valuable properties indicated below. A heavy hydrocarbon gas is produced by the conversion of a heavy hydrocarbon oil in such a manner that as large portions as practicable of the product of conversion consist of the heavier hydrocarbon gases, and as small a proportion as practicable, consist of the lighter and more permanent gases such as methane and ethane. These heavier gases can be produced in large proportion by taking care not to perform the gasifying at too high a temperature and not to expose the gases to high temperature for too long a space of time; for, if the heavier gases be superheated, they have a tendency to decompose further into the lighter gases which are much less desirable. It is found that a solution of these heavy gases in alcohol constitutes an excellent motor fuel which permits starting the engine with ease

[1] J. S. C. I. 1915, 414; British Patent 2948, February 4, 1914.

even in cold weather, besides giving elasticity and excellent acceleration in running. These gases held in solution in the alcohol show but little tendency to escape; even at the boiling point of alcohol a considerable quantity, it is maintained, still remains in solution; the solution has a much lower flash point and initial boiling point than is possessed by alcohol, and has a higher vapor pressure and greater thermal value. The product also has larger fractions volatile at low temperatures.

H. W. Wiley [1] states that alcohol can be used for all purposes for which gasoline is employed. Very little change need be made in the engine of a motor car designed to use gasoline to fit it for the use of alcohol. Gasoline becomes volatile at a temperature of blood heat (98.5° F.), while a much greater degree of heat (158° to 176° F.) is necessary to volatilize alcohol rapidly enough for motor purposes. This fact makes necessary a change in the engine when alcohol is to be used This adjustment is especially important in the starting of the machine, as after it is in action the temperature of combustion is quite sufficient to easily produce the gasification necessary.

In the driving of motor engines the quantity of heat evolved is not always a measure of efficiency. The vapor of alcohol can be more highly compressed at any given temperature without exploding than can the vapor of gasoline. As the decreased volume of the mixture of the explosive vapor and air is to a certain extent a measure of efficiency when engines are driven by the expansion of gases, the high degree of compressibility of the alcohol vapor without danger of explosion may compensate for the smaller quantity of heat which is generated by its combustion

In the exploitation of tax-free alcohol extravagant opinions regarding its possibilities have, it is said, been expressed. These exaggerated statements have been made without any intent to deceive or mislead, but on account of insufficient information. The natural tendency in all such matters is to select those points which are certain to be of great benefit and publish them broadcast, and to neglect the difficulties and dangers which lie in the path of progress along these lines Those who are naturally conservative need very little caution in such matters, but it is important that a full understanding of the difficulties of these problems should be disseminated It is quite certain that if alcohol can be produced in the near future at a cost not exceeding 25 or 30 cents per gallon of 95 per cent strength, it will be a most valuable source of power. With the present relative prices of alcohol and gasoline there is no financial advantage in the use of the former.

Commenting on the future of motor spirit **V. B. Lewes** [2] notes that the increase in consumption of gasoline is out of proportion to the increase in production of crude oil. Lecturing at the Royal Society of Arts in London (J. Ind. Eng. Chem. 1915, 999) he stated that the world's total output of crude oil, which in 1914 amounted to 97 million tons, had, he said, increased at an annual rate of only 6 per cent for the past three years. America itself used 1,200,000,000 out of the world's 1,700,000,000 gallons and England in 1914 imported 120,000,000 gallons,

[1] U. S. Dept. of Agriculture, Farmers' Bulletin 269, 1906.
[2] J. S. C. I. 1913, 411; Chem. World, 1913, 2, 111–113.

making a total of 1,320,000,000 gallons, leaving only 380,000,000 gallons for the remainder of the world.

It was stated also that in the next, say 50 years, the natural supplies would be diminished to such an extent that the depth from which the oil would have to be obtained would render these sources practically commercially unavailable.

It was Professor Lewes' opinion [1] that crude oil cannot be a lasting source of supply of motor spirit and that the motor spirit of the future will be alcohol in admixture with benzol.

For a number of years Great Britain has been endeavoring to make herself economically independent as regards supplies of motor fuel and is turning to alcohol as one of the substances which promises to solve this problem to a large extent, in conjunction with the benzol obtainable from her coke ovens.

Grady [2] refers to the report of the British Inter-Department Committee on the Production and Utilization of Power Alcohol recommending the establishment of a Government organization to initiate and supervise experimental and practical development work on the subject, and the London *Times* states that such an organization, with funds, is to be set up under the Department for Scientific and Industrial Research.

The report also refers to the possibility of obtaining large supplies of alcohol synthetically from the products of coal distillation The gases produced from gas retorts and coke ovens contain about one-half of 1 per cent by weight of ethylene, and a process is being worked out for collecting this ethylene and converting it into alcohol. For extracting it, use is made of the property possessed by cooled charcoal of absorbing gas, and the charcoal, when charged with the gas, is carried in a stream of molten lead, the heat of which causes it to give up the ethylene, which is then treated catalytically for the production of alcohol.

Could Retail at 30 Cents a Gallon. --- The amount of ethylene in the gas works and coke-oven gases of Great Britain is estimated to be sufficient to yield annually up to 150,000,000 gallons of 90 per cent alcohol, which it is said, the manufacturer could afford to sell for 1s. 3d [30 cents] a gallon; and even if it were found practicable, owing to such difficulties as that of collecting the ethylene from all the gas works (many of which are small and are situated in remote districts) to treat only half the total produced, some sixty or seventy million gallons would be obtained. Already several important collieries are believed to have in hand the addition of conversion plants to their existing coke oven installations.[3]

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[1] *Ibid.*   [2] Commerce Reports 1919, Sept. 18, p. 1460, et seq.

[3] In Great Britain gasoline (petrol) and benzol, as sources of motive power, have hitherto held the field on account of their relative cheapness, although the production of synthetic alcohol from calcium carbide and from coke oven gas is considered by **C. Simmonds** (Alcohol: Its Production, Properties, Chemistry, and Industrial Applications, London: Macmillan & Co., Ltd., 1919; J. S. C. I. 1920 46, R) to bid fair to assume noteworthy proportions in the not far distant future, and there is evidently approaching a period of keen competition between the existing available sources of energy, in which alcohol will play an increasingly important

Alcohol by itself, as has previously been noted, is not suitable for use in existing types of high-speed internal-combustion engines, but mixed with an equal amount of benzol it forms an excellent fuel for the purpose. Some difficulty in starting the engine in cold weather is a disadvantage. The production of 90 per cent benzol in England is about 31,000,000 gallons annually, and may in the near future be increased to 50,000,000 gallons or more. Hence, if the hopes of synthetic alcohol are realized something like one-half of the present requirements of gasoline in the United Kingdom may be obtained from British sources, in the shape of alcohol-benzol mixtures

Numerous Vegetable Sources of Alcohol.[1] —The outstanding and fundamental attraction of alcohol motor fuel as a substitute for any fuel necessarily derived from coal or oil deposits lies in the fact that on account of its chief sources being found in the vegetable world, supplies of raw material for its manufacture are being continuously renewed and are susceptible of great expansion without encroachment upon food supplies. The following items are taken from the report of the interdepartmental committee.

Steps should be taken to insure increased production of power alcohol by the extended use of the vegetable matters from which it may be obtained. Important materials of this nature are (1) Sugar-containing products, such as molasses, mahua flowers, sugar beets, and mangolds; (2) starch or inulin-containing products, such as maize and other cereals, potatoes and artichokes; and (3) cellulose-containing products, such as peat, sulphite wood-pulp lyes, and wood. . . .

Evidence from the Director of Commerce and Industries concerning achieved production costs and yields of power alcohol from the flowers of the mahua tree (*Bassia latifolia*), which flourishes in the Central Provinces as well as in Hyderabad affords this information: the sun-dried flowers of this tree contain on the average 60 per cent by weight of fermentable sugar, and they can be collected and delivered to the factory in the zone of growth at $7 25 per ton. The yield on proper fermentation and distillation is found to be about 90 gallons of alcohol (95 per cent by volume absolute) per ton. The flowers can be pressed, packed, exported, and stored for long periods without deterioration Cultivation of the mahua tree has not as yet been attempted, and there may therefore be possibilities of increased production of flowers by cultural treatment

The large-scale cultivation of corn and other cereals as raw material for the manufacture of power alcohol has admitted possibilities, and it would appear that prospective production of alcohol from these sources in the overseas Dominions and other parts of the Empire is encouraging both as regards quantities and cost.

part The eventual exhaustion of the world's supplies of coal and mineral oil may well have the effect of stimulating the development of the agricultural resources of tropical countries, which, Simmonds asserts, should be capable of furnishing an almost inexhaustible supply of fermentation alcohol.

[1] In discussing sources of alcohol, **E. K. Rideal** (Chem. Age, 1919, 1, 9; Chem. Abs. 1919, 3184) refers to the hydrolytic conversion of wood cellulose into sugars, accomplished by the catalytic action of acids. The sugars undergo fermentation to alcohol and carbon dioxide. The insoluble wood fiber, a by-product, is suited for the manufacture of papier mache. The great dilution of the sulphite liquor from paper mills makes its conversion to alcohol at present uneconomical. The economic conversion of ethylene to alcohol, Rideal thinks depends on the catalytic acceleration of the hydration of ethylene which is unsolved at present.

Seeing that 1 ton of potatoes yields only 20 gallons of 95 per cent alcohol, while the yield from artichokes is only very slightly higher, the committee is of opinion that, having regard even to the pre-war prices of potatoes and artichokes in the United Kingdom, power alcohol cannot be produced in that country from these sources on a commercial basis except under some system of State subvention. Similar considerations apply also to the sugar-beet and mangel crops.

No satisfactory method for the utilization of peat as an economic source of power alcohol has been brought to notice In connection with researches into the use of peat for various purposes its potential value as raw material for the manufacture of alcohol should not be overlooked.

So far as vegetable sources of raw material for the manufacture of power alcohol are concerned, the committee believes Great Britain must rely mainly, if indeed, not entirely, on increased production in tropical and subtropical countries.

General Recommendations. — The general recommendations of the committee are as follows:

The time has come for action by the Government to insure close investigation of the questions of production and utilization, in all their branches, of alcohol for power and traction purposes.

In the British Empire there are vast existing prospective sources of alcohol in the vegetable world, although in the United Kingdom itself production from these sources is now and is likely to remain small, but synthetic production in this country in considerable quantities, especially from coal and coke-oven gases, is promising.

As the price of alcohol for power and traction purposes, to which the name of " power alcohol " may be given, must be such as to enable it to compete with gasoline, it is essential that all restrictions concerning its manufacture, storage, transport, and distribution should be removed so far as possible, consistent with safeguarding the revenue and preventing improper use, and that cheap denaturing should be facilitated.

An organization should be established by the Government to initiate and supervise experimental and practical development work, at home and overseas, on the production and utilization of power alcohol, and to report from time to time for public information on all scientific, technical, and economic problems connected therewith. This organization should be permanent, have at its disposal the funds necessary for its investigations, be in close relation with the various Governments of the Empire, and be so constituted as to be able to deal with alcohol in conjunction with other fuels which are or may become available as a source of power.

Steps to facilitate the production and utilization of power alcohol in the United Kingdom can in no circumstances be taken, nor arrangements for such development carried into effect, unless provisions and alterations of the kind recommended are made in advance of the time when an acute recurrence of high prices for motor fuels may otherwise call for action too late for it to be effective.

Details of the method of producing alcohol from the ethylene of coke-oven gases are furnished by **E. Bury** and **O. Ollander.**[1] The normal amount of ethylene and its homologues present in coke-oven gas from Durham coal is approximately 2 per cent by volume, so with a 70 per

[1] Gas J. 1919, 148, 718; Chem. Trade J. 1919, 66, 36; Iron & Coal Trades Review, 1919, 99, 804; Chem. Abs. 1920, 826.

cent absorption of this gas as ethyl sulphuric acid with a 70 per cent conversion of the latter to alcohol a yield of 1.6 gallons of absolute alcohol would be obtained per ton of coal. During the war, research was made at the Skinningrove Iron and Steel Works toward the recovery of ethylene from coke-oven gas, the ethylene being utilized for the manufacture of mustard gas by passing it directly into sulphur chloride. It was shown that after purifying the gases of hydrogen sulphide, carbon bisulphide and carbon dioxide the heavy hydrocarbons could be readily removed. Peat, or beech charcoal, was proposed as the absorbent and the ethylene driven off by heating. Later 95 per cent sulphuric acid was deemed preferable as an absorbent on these grounds:[1] (1) Sulphuric acid can be obtained from the coal itself independently of outside resources. (2) Handling charcoal on such a system is much more costly than pumping a liquid. (3) To use charcoal the carbon dioxide must be removed from the gas; otherwise the carbon dioxide is absorbed instead of the ethylene. (4) Heating the charcoal requires a greater expenditure of heat than the direct heating of sulphuric acid. (5) Charcoal will absorb only 1 per cent of its weight before losing its efficiency, whereas sulphuric acid will absorb 5.1 per cent of its weight. A disadvantage of using sulphuric acid is that a considerable amount of it, after absorption of ethylene, is reduced to sulphur dioxide which, unless recovered, adds to the cost of the process. As to the efficiency of the absorption Fritsche had formerly stated that 12 cu. m. of scrubbing surface were required per cu. in. of gas treated per minute and that even under higher pressures than 4 atmospheres the degree of absorption could not be increased. It was finally ascertained that, given sufficient scrubbing surface, 70 to 80 per cent of the total ethylene can be absorbed by 95 per cent sulphuric acid at temperatures between $60°$ and

[1] Lebeau and **Damiens** have shown that in the presence of catalysts such as vanadic, uranic, tungstic, or molybdic acids, sulphuric acid rapidly and completely absorbs ethylene (J. S. C. I. 1913, 277), and it has since been shown by Damiens that the ethylene is absorbed as ethyl hydrogen sulphate. **E. de Loisy** (Comptes rend 1920, 170, 50; J. S. C. I. 1920, 147A) makes use of these two important facts in his process. The coal gas is bubbled through the acid at a concentration of $66°$ Bé, and by suitable subsequent dilution and distillation alcohol or ether may be obtained as required. The diluted acid serves for the preparation of ammonium sulphate. Since, however, twice as much acid is required for the absorption of ethylene as for the production of ammonium sulphate, a portion of the acid is concentrated by means of the waste heat from the gas coming from the coke ovens, and can thus be used either for the absorption of the ethylene or for the preliminary drying of the gases and the absorption of the traces of propylene, butylene, and acetylenic hydrocarbons present. By this method it is only necessary to replace the acid removed in the form of ammonium sulphate. (See also Bury, J. S. C. I. 1920, 94A.)

80° C., also that 71 per cent of the total is removed in two minutes. Temperatures higher than 80° C. cannot be used, as decomposition occurs, while below 30° C. the recovery is almost negligible. Water must not be present in the sulphuric acid nor in the gas, else absorption of ethylene fails, and the ethyl sulphuric acid already formed hydrolyzes *in situ* forming ethyl alcohol, which is carried forward in the gas. In developing the process further two ways were presented:' (1) Oxidation of ethyl sulphuric acid by electrolysis for the manufacture of acetic acid, (2) hydrolysis with superheated steam for manufacture of alcohol and the recovery of the sulphuric acid. By the former method 80 per cent of the acetic acid may be obtained, by the latter 70 per cent of the ethyl alcohol, the main problem being the limit of dilution of the acid with water, the sulphuric acid being reconcentrated for re-use in the ethylene scrubbers. The 95 per cent sulphuric acid is reduced by the absorption of ethylene to 77 per cent, and by the distillation of the alcohol formed during the hydrolysis to 74 per cent. This figure should be improved in the commercial process with more efficient apparatus. The sulphur dioxide present in the exit gases can be recovered by passing the exit gases back into the coke-oven gas and precipitating sulphur according to the reaction $2H_2S + SO_2 = 2H_2O + 3S$, thus not only purifying the oven gas and preventing loss of sulphur dioxide but providing the sulphur for making sulphuric acid for the process and for the manufacture of ammonium sulphate. Economy in fuel is obtained by utilizing the waste heat in cooling the gas from 250°–300° C. down to the required 60°–80° C. The removal of the ethylene does not materially affect the calorific value of the gas since the ethylene extracted represents only 4.7 per cent of the total calorific value of the average gas.

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CHAPTER XXVI

SHALE AS A SOURCE OF MOTOR FUEL

In considering shale as a source of motor fuel, the following questions especially should be reviewed: (1) Of the crude oil obtained, what percentage of light naphtha can be obtained by straight distillation? (2) How much of this can be produced in a condition suitable as motor fuel? (3) What proportion of the waste oils, that is, gas oil and even heavy residues occur in distilling? (4) How much light naphtha can be produced by augmenting the straight distilled naphtha with naphtha produced by cracking the heavier oils (including burning oil, gas oils, etc., and even fuel oils)?

In other words we will consider the yield and chemical quality, not only of the naphtha, directly obtainable, but also of the burning oils, gas oils and other hydrocarbon oils, because it will be possible to convert the heavier hydrocarbons into lighter ones by cracking methods. Mining methods and retorting processes (of which there are many) will be considered briefly.

A short account of the chemistry of the organic matter in shale is also given as this is believed to be of fundamental importance to an understanding of the peculiar characteristics of shale oil and wherein it differs from petroleum.

A great deal of interest has been of late shown [1] in various parts of the world in connection with the production of gasoline substitutes from shales rich in hydrocarbons. The United States Geological Survey has investigated these deposits, the largest of which are found in the Green River formation of northwestern Colorado and northwestern Utah. These areas have been mapped out, their depths and lengths have been measured, and crude field tests made. The shales on distilling yield petroleum, the amount depending largely on the richness in hydrocarbons of the shales, which varies in different localities. In the United States Geological Survey Press Bulletin for December, 1916, it is stated that in Colorado alone 20,000,000,000 barrels of crude oil could be obtained by distilling shale deposits ranging over 3 feet in thickness. This would yield, it is said, in the neighborhood of

[1] Anon. Met. and Chem. Eng. 1917, 16, 71.

2,000,000,000 barrels of gasoline substitute, an item of considerable
importance.[1]

The oil produced from some of these shales is dark brown in color, rather
mobile, and has a dominant odor of the lighter hydrocarbons. The extent to
which these latter are present may be judged (it is stated) from the fact that on
receiving a sample directly from the source of distillation it was put in a bottle
and stoppered very tightly with an ordinary cork. After standing for three weeks
the oil had become very viscous, had very little odor due to the lighter hydro-
carbons, the main odor now being that typical of the product left on distilling
ordinary petroleum for the lighter and more volatile constituents.

Rich oil shale is stated to be very tough, burns on ignition and resists, to a
remarkable extent, erosion. On weathering a bluish white color is developed.
A good oil shale should be dense in structure and flatten out to an adhering mass
on pressing a small piece with the blade of a knife. Colorado oil shales yield a
crude oil which gives 10 to 15 per cent gasoline by ordinary methods of refining
Furthermore, 300,000,000 tons of ammonium sulphate, it is said, could be derived
from the Colorado shales. This product is of exceptional value as a fertilizer
The equipment for a plant handling these shales would be rather costly and com-
prise buildings, retorts, condensers, refining machinery and mining machinery. The
oil shale industry on a small scale would in all probability not pay."

Regarding the use, as motor fuel, of shale naph'ha, **J. V. Meigs** [2]
recommends improving the latter by the solution therein of a suitable
proportion of alcohol in order to assist in overcoming the tendency of
the unsaturated hydrocarbons in shale naphtha toward carbon deposit
when burned in automobile cylinders. He points out that such a
procedure would bring together two of our largest future motor fuel
sources, viz. alcohol and shale oil.

The economic success of a shale-oil industry, **Baskerville** [3] finds, will
depend upon the following factors: (1) The shale must yield an oil
of satisfactory character, resembling petroleum of good quality. (2) The
oil must be produced in sufficient quantity to pay costs of mining,
retorting and refining, or must be of unusual value because of high

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[1] South Africa seems to offer another possible source for gasoline from bitu-
minous shales. According to the South African Mining Journal, Aug 19, 1916,
p. 460, such bituminous shales should not occur in metamorphic rocks, because
any severe metamorphism destroys these shales. Bituminous shales are known
to occur in the Black Shale group in Rhodesia The deposit lies in the region
of the Wankie Main coal fields. Other possible localities in South Africa are stated
to be the main belt which stretches in a northeastern and southwestern direction
through the Wankie and Sebungwe districts. **Du Toit** (South African Mining Jour-
nal, Oct. 28, 1916; Met. and Chem. Eng. *loc. cit.*) states that he has examined shales
which produced 27.1 gal. of crude oil per ton of shale. On the other hand, reports
have it that shales giving a far greater amount of crude oil have been tested.

[2] Address delivered before New Jersey Chemical Society, Newark, N. J., April
12, 1920.

[3] Chem. Abs. 1919, 2126; Bull. Am. Inst. Mining Met. Eng. 1919, 957–60.

content of paraffin or ichthyol.   (3) The yield of ammonia must be relatively high.   (4) The shale must be abundant, and capable of being mined cheaply.   Abundant water supply of good purity is necessary.   (5) An adequate supply of (cheap) sulphuric acid is essential.   A 50,000,000 barrel annual production of shale-oil would require, it is said, 625,000 tons of sulphuric acid yielding over 800,000 tons of ammonium sulphate.   This quantity of sulphate would materially effect the market price.   (6) Proper methods of retorting for such shale are essential. Full-size plant test operations give the only reliable results.   Much investigation is stated to be still necessary for successful plant practices.

Simpson [1] states that Scotch retorts have been brought to a high degree of perfection for treating Scotch shales, under the very special industrial, commercial, financial and climatic conditions which exist in Scotland.   It does not follow, however, that these designs of retorts are the most suitable for other shales and other conditions.   Too many tests have been made with Scotch retorts by Scotch engineers upon the assumption that the success or failure of the runs would be indicative of the advisability of developing the industry in other localities.   The most desirable practice in retorting with especially designed retorts requires application of the following principles: — Continuous feeding of dried shale, continuous removing of spent shale, heating by means of preheated gas, avoiding the high temperatures of the Scotch retorts themselves, conserving all heat possible, removing educed gases as quickly as possible, condensing the educed gases at constant speed conditions, giving, by such condensation, oils fractionated into four or more kinds, and washing with an efficient washer which requires infrequent cleaning.   The ground area of the plant should be small.   The buildings should be of fireproof construction.   A plant for 1000 tons per 24 hour day, including everything but storage tanks, should not, it is said, cover more than 2500 square feet.

Winchester [2] notes that although the first steps toward the commerical development of oil shale in the United States were taken only a few years ago, there are at the present time prospects that within another five years, an industry of immense proportions will be well started and commercial production of shale oil may have assumed considerable proportions.

D. R. Stewart [3] observes [4] that the Boghead or Torbanehill Mineral

[1] Chem. Abs. 1919, 2592; Chem. Met. Eng 1919 (21), 176-8.
[2] Chemical Age, 1919, 119.
[3] "The Chemistry of the Oil Shales" in "The Oil Shales of the Lothians" (Scotland) being part of the Memoirs of the Geological Survey, of Scotland.   2nd Edition.   Edinburgh.   Morrison and Gibb, Limited, 1912.
[4] Ibid. p. 160.

was the first substance used in Scotland for paraffin oil making, and torbanite is by far the best yet discovered for that purpose or gas making. There is some question as to whether torbanite should be regarded as coal or shale, and in a strict scientific sense probably should be termed a very rich shale.

It is further stated[1] that in the oil-shale, as in the Torbanehill Mineral, paraffin and paraffin oil do not exist as such: they are created by the destructive distillation in the retorts. There is very little in shale soluble in petroleum spirit, benzene, carbon disulphide, ether, and such solvents. The substance is therefore, it is stated, not of the nature of petroleum, bitumen or resin. All hydrogen and carbon compounds produced by inorganic reactions are soluble in these solvents, and this makes it almost certain that kerogen is of organic origin.

The material has probably been deposited, it is said, together with clay, at the bottom of lagoons, and has there been subjected to maceration and limited microbe action. Part would decompose and only what could withstand the water, etc., would remain. According to Stewart, we can imagine a plant or plant-organ decaying and leaving only the wax or fat that was originally meant for its protective covering, or perhaps some resinous excretion or secretion But this would give materials soluble in solvents, and might account for the origin of petroleum or bitumen, but not for kerogen.

Some shales are largely made up of entomostraca, and it is probable[2] that the animal matter has in some cases been converted into kerogen. Kerogen can be conceived as produced from any kind of organic matter by the action of microbes under special circumstances, the product being dependent on the microbe. Or, on the other hand, kerogen in some cases may be the remains of certain kinds of vegetable matter, like pine pollen or lycopod spores, perhaps little altered, the product being dependent on the nature of the original organic matter. Surmising that kerogen might be some such substance not much altered, it was endeavored to make artificial shale. Dried Florida fuller's earth was taken, 75 parts, and lycopodium spore dust, 25 parts, to represent the supposed lycopodiaceous *Lepidodendron* spores from forests by lagoons, and the mixture was moistened and made into a brick with gentle heat. It was then broken up and distilled in a laboratory retort. Crude oil was obtained equal to 23.8 gallons per ton, sp. gr. .930, and setting point 35° F. (2° C.), and sulphate of ammonia 3.3 lbs. per ton. It was found, however, that lycopodium dust, treated with benzene C_6H_6, Soxhlet fashion, gave up 21 per cent in solution, which, on evaporation of the benzene, yielded a yellow-brown viscous oil. After thorough extraction of the oil in this way, the remaining insoluble matter of the spore dust was taken and made into a brick as before, and in the proportion of 25 per cent of the original dust. On retorting, crude oil was obtained equal to 17 gallons per ton, sp. gr. .930, and sulphate of ammonia 1 lb. per ton. The crude oil, specific gravity and setting point, and the amount of ammonia agreed very well with the figures got from the Torbanehill Mineral and the higher shales.

Others have ascribed the organic matter in shale to lycopodiaceous spores, and it is quite reasonable to consider that such material contributed to some extent at least to the formation of the Torbanehill Mineral and oil-shale. As peat gives paraffin products on distillation very like those of shale, it is probable that

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[1] *Ibid.* pp. 164–165. [2] **Stewart,** *loc. cit.*

shale contains ordinary vegetable or organic matter that has undergone decay to substances of a humic acid nature, which have been rendered insoluble and preserved by chemical combination with the metallic oxides of the clay or water, the alumina, lime, etc.

Oil-shale, therefore, may be composed of (1) vegetable matter which has been made into a pulp by maceration in water and preserved by combining with the salts in solution as already mentioned; (2) richer materials of many kinds, such as -pores, which nature has provided with means for protection against decay; and (3) a proportion of animal matter.

Again, shale may be considered as torbanite containing a larger proportion of earthy matter from its original deposition, or perhaps shale is simply a torbanite that has deteriorated with age. For, as already indicated, the crude oil diminishes and the ammonia increases as a general rule with the age of the shale. In old peat the proportion of nitrogen is sometimes, if not always, greater than in new peat of the same bog, owing to the nitrogen-free compounds decaying more rapidly than the nitrogenous compounds under the special circumstances Recent plants subjected to destructive distillation yield a very acid distillate, peat less so, brown coal still less, Torbanehill Mineral has a distillate slightly acid at the beginning and alkaline further on, while shale is very alkaline throughout Hence the decrease of crude oil and increase of ammonia may partly be the result of age No doubt part of the nitrogen is in combination in the kerogen,[1] and this part may through time have increased in proportion; but the richness of the older shales in ammonia is more, it is stated, than we would expect from this cause alone.

Winchester (*loc. cit.*) believes that it has been pretty definitely proved that the oil shale of the Green River formation to be found in Colorado, Utah and Wyoming does not contain oil as such but does contain partly bituminized vegetable matter in such a state of alteration that the addition of heat will produce oil.

[1] The composition of the organic constituents of good average shale, representing the kerogen referred to, is given by **Mills** (Destructive Distillation, 4th Edition, p 50). --

Carbon	25 27	per cent
Hydrogen	3 67	"
Oxygen	5 65	"
Nitrogen	1.14	"
Sulphur	0 49	"
	33 22	"

Part of the nitrogen and sulphur are no doubt in combination in the kerogen; but excluding the ash, nitrogen and sulphur, the percentage composition is:—

Carbon	73 05
Hydrogen	10 62
Oxygen	16.33
	100 00

This corresponds to $C_6H_{10}O$.

The proportion here between carbon and hydrogen is 100 carbon to 14.5 hydrogen.

The flexibility of oil shale distinguishes it, according to **Winchester** [1] from ordinary carbonaceous shale which is brittle. Freshly broken oil shale gives off a peculiar odor similar to that of crude petroleum, although the shale contains, it is said, little oil as such or bituminous matter that is soluble in ether, chloroform, carbon bisulphide or other solvents for bitumen. It is stated [2] that experiments have shown that from a sample of shale yielding oil to the extent of 14 per cent of its weight (by distillation) it is possible to extract from the original shale by means of carbon bisulphide less than 10 per cent of the amount of oil obtainable by distillation. The large ash content of shale (for example, that from the Green River formation in Colorado, shows [3] an average ash content of 60 per cent) renders it impossible to use the crude shale directly as fuel. It must therefore be distilled in order to obtain shale oil, fuel gas, ammonia and other nitrogen compounds (for example, pyridine).

Fractionation of shale oil in Northwestern Colorado and adjacent area gives the following products [4] as oils.

Gasoline (distillate to 150° C.)	.	7–12 0 per cent
Kerosene (150–300° C.)	.. .	28 5–49 0 per cent
Asphalt	.	0 47–4 1 per cent
Paraffin	. .. .	1 63 9 21 per cent

A small amount of " shale spirit " may be obtained from the permanent gas derived in the original distillation, but most of the valuable hydrocarbon products will be produced from the shale oil itself.

Tests conducted in the laboratory and in small experimental plants show [5] that in this country layers of shale, mostly, however, too thin to mine commercially can be obtained that will yield upwards of 90 gallons of oil a ton, and that there are extensive deposits of shale several feet thick — at least one being reported at 25 or 30 feet — that will yield, according to small-scale tests, one barrel (42 gallons) a ton. It must be understood, however, that the quantity and quality of oil that can be obtained from a given shale will depend to a considerable extent on the methods used in obtaining the oil; the types of retort, rate of heating, removal of vapors, etc. It is also difficult to get a small sample that truly represents a workable deposit. In Scotland testing methods have been worked out which give results comparable with those obtained in commercial plants in so far as quantity of oil and ammonia recovered is concerned. If proper care is taken

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[1] U. S. Geological Survey Bulletin 691–B, p. 40 (April 30, 1918).
[2] Winchester, *loc. cit.* p. 41.   [3] Winchester, *loc. cit.*
[4] Winchester, *loc. cit.* p. 43.
[5] U. S. Bureau of Mines. Notes on Oil Shale Industry with particular reference to the Rocky Mountain district, p. 3 (May 1, 1919), by Gavin. Hill and Perdew.

in sampling such tests may be expected to furnish valuable information relative to yields of oil and ammonia.

Investigations by the United States Geological Survey indicate that, in the Rocky Mountain States, there are enormous quantities of oil shales which can be made to yield hydrocarbon oils to a much greater extent than we can hope to obtain from our oil wells.[1]

Our oil shales thus constitute a tremendous potential reserve. While oil can readily be obtained from these shales, it has not been demonstrated in actual commercial practice whether it can be produced with profit under the conditions obtaining in the United States today. A distinction must be made between the possibilities of local commercial developments under most favorable local conditions and the development of the industry on a sufficiently large scale to supplant in large part the petroleum industry. The latter is obviously many years ahead and must necessarily be the outgrowth of local industries started under rather exceptionally favorable conditions. The question at the time is when and where such local industries can be started. There are to be considered, therefore, the broad questions of technique of mining and retorting shales and the refining of shale oils, as well as the economic considerations of costs and marketing of products. Much remains to be done in the technique of the industry, as it has not been established that the Scotch practice can be adopted in toto or that it is the best for American conditions. Still more remains to be done in establishing reliable cost data and value of products and possible by-products.

Technical Considerations [2]

Preparing Oil Shale for Distillation. — After oil shale is mined and brought down to the plants for the manufacture of shale oil, it needs to be crushed before it is subjected to distillation, and the fineness to which it is crushed will depend on the method of treatment to which it is to be submitted. The existing machinery for crushing rock may need to be remodeled to handle efficiently and economically this tough, almost rubbery shale, which is inclined to pack rather than to crush but this is a minor mechanical detail which can be adjusted.

Distilling Machinery

At the present time there is a great amount of activity in shale distillation, particularly in the States of Colorado, Utah, and Nevada, where there are large and easily accessible deposits of rich oil shale and where geographic and transportation conditions are such as to favor the production of oil in these states.

The manufacture of the shale oil and by-products from oil shale requires heat, and many types of apparatus are being designed and

[1] U. S. Bureau of Mines. Notes on Oil Shale Industry, May 1, 1919, p. 4.

[2] Condit, U. S. Geological Survey, Bulletin 711–B, pp. 37–40; from contributions to Economic Geology, 1919, Part II, pp. 15–40.

tried. At least twenty processes for the extraction of oil from shale are recognized.

In order to obtain the maximum amount of ammonia in the shale it is necessary, according to Condit, to heat the shale to incandescence and then to introduce steam. The steam dissociates in the presence of fixed carbon which has been formed in the process of heating, liberating hydrogen which combines with the nitrogen, forming ammonia. In this country, where our most favorable shale deposits are very much richer in oil, but contain less nitrogen than the Scottish shales, it may prove advantageous to neglect more or less the ammonia production and to increase the capacity of a plant by shortening the time and temperature of heating.

Theoretically, all the products now obtained from both crude petroleum and from coal tar are possible from shale oils. The Scottish operators have never made many different products from their shale oil, marketing it as motor spirit, naphtha, burning oil, gas and fuel oil, lubricating oil, and paraffin wax. This is probably largely due to the fact that they have well-established markets for these products and for this reason find it more profitable to confine themselves to them. It must be realized that no little skill and experience will be necessary in making many different marketable products from shale oil.

Costs. — The cost of mining oil shale will probably be as great as that of the mining of coal in the same general region under similar conditions, if not greater, and underground mining will therefore cost at least $1 a ton.

Reliable general estimates of the cost of shale oil operations can not be made, as most of the costs are dependent largely on local and individual conditions. Some of the shale deposits are such that the shale can be mined with a steam shovel. This, of course, is a much cheaper method of mining than the stope and pillar or other methods where the shale must be brought from underground. Thirty-five cents per ton is considered by some as a reasonable figure for the average steam-shovel mining and $1.15 per ton as an average figure for underground mining.

The delivery of oil shale to the retorts will in most places necessitate the installation of tramway systems. Crushers of special types will be needed to reduce the oil shale to proper fineness for retorting. The original cost as well as the cost of operation of crushers will depend largely on the degree of pulverization demanded by the retorts in which the shale is to be distilled, but in any case the cost will not be small.

The estimates of cost of installing the various retorting systems range from $300 to $2500 per ton of shale to be handled daily. These figures

represent preliminary estimates, and in the present state of the industry they are the best available. Accurate figures relative to the costs of operating the retorting machinery will not be available until plants of commercial size are put into operation. The cost, in Scotland, of a commercialized Pumpherston plant complete with retorts, condensers, and ammonium-sulphate house was estimated by Henderson [1] at pre-war prices (before 1909) to be at least $350 per ton of shale to be treated daily.

After the oil shale has been mined, prepared, and retorted, the product is crude shale oil, which, like crude oil-well petroleum, must be refined before its value will be fully realized. A refining plant must therefore be available, and tank cars or trucks will be needed for transporting the crude shale oil to the refinery, as there seems to be ample indication that it will be impractical to convey shale oil by pipe line because of the fact that the oil may be thick or almost solid, at least in cold weather. The shale oil manufactured in Scotland is too thick for piping at ordinary temperatures.

It is evident, therefore, that the installation of a commercial oil-shale plant means the expenditure of no less than half a million dollars and probably much more, and such a plant must be operated with the greatest efficiency and at a minimum cost in order to produce shale oil and other oil-shale products at a profit. The production of shale oil in paying quantities will require plants capable of treating great amounts, perhaps 1000 tons of shale a day. If it is assumed that the average oil shale treated will yield approximately 1 barrel of shale oil per ton of shale, it will be necessary to install and operate a great number of such plants to enable the shale-oil industry to replace in any great degree the decreasing supply of petroleum in this country.

The pre-war cost of retorting in Scotland was about forty cents a ton, but to accept that figure, without modifications in making estimates of present charges, is not justifiable, as labor and material costs, even in Scotland, are much higher than they were before the war.[2]

Estimates by various engineers of the cost of a complete retorting plant, handling 1000 tons of shale a day, are between $1,000,000 and $5,000,000, and if the average shale treated yielded 42 gallons of oil a ton it would probably require at least 1300 such plants to supply the volume of crude oil that is being consumed in this country today, and the shale mined daily would amount to approximately one-half the coal mined daily in this country. However, it is hardly to be expected

[1] Ells, R. W., Joint report on bituminous or oil shales of New Brunswick and Nova Scotia, p. 29, Canada Dept. Mines, 1909.

[2] U. S. Bureau of Mines, Notes on Oil Shale Industry, May 1, 1919, p. 10.

that shale oil will be called upon to replace petroleum completely, for a great many years. Although the Scotch industry has been existent for more than 50 years, the amount of shale oil produced in Scotland during the calendar year of 1916 was less than three days' average production of crude oil in the United States during the same year.[1]

It is stated that until the shale oil industry has assumed large proportions it must depend upon local markets under the local competitive conditions that prevail during that period.[2] At the present time the chief competition will be from products obtained from the oils of the Wyoming oil fields which marketed over 12,000,000 barrels of high grade crude oil in 1918, then selling at about $1.80 a barrel at the well. The oil shale plants in Scotland are located very favorably, for they are near the two largest cities of Scotland and compete with petroleum products that must be imported from the United States and other foreign countries.[4]

The U. S. Bureau of Mines [4] notes that it costs in round numbers about ten cents per barrel to " top " crude oil, that is, take the gasoline off crude oil, and that it seems reasonable to believe that shale oil can be topped at about the same cost.

Winchester [5] in six tests to determine the comparative values of steam and dry distillation on the yield of oil from shale in Colorado and adjacent areas, found with four out of the six samples (from the same lot of shale) that steam causes an increased yield of from 10 to nearly 50 per cent over that obtained with dry distillation. In the other two tests about the same amount of oil was obtained.[6]

From the examination of a large number of samples, the following yields of the various fractions were obtained:

Gasoline	... . 6–12 per cent
Kerosene	.. ..28 5 49 per cent
Paraffin	. .. .1 63 -7 70 per cent

Sulphur in the crude oil was found to range from 0.41 to 1.42 per cent. It is also stated that samples of oil subjected to cracking showed that

[1] U. S. Bureau of Mines, Notes on Oil Shale Industry, May 1, 1919, p 13.

[2] U. S. Bureau of Mines, loc. cit., p. 13.

[3] **V. B. Lewes** (J. S. C. I. 1913, 411; Chem. World, 1913 (2), 111 -113), states that the Scotch shale oil industry yields about 600,000 gallons of motor spirit per annum.

[4] Chemical Age, 1919, 124.

[5] Chem. Abs. 1917, 1808–9; U. S. Geological Survey, Bulletin 641–F (1916), 139–98.

[6] Steam distillation of shale increases the yield of the oil a few gallons per ton, and the specific gravity of the oil thus obtained is higher by 0.03 to 0 04 than when a dry distillation is made according to **C. W. Botkin** (Chem. Abs. 1920, 1753; Quarterly Colo. School Mines 4, No. 4, 16–17 (1919)). The yield of ammonia is increased to 2 to 3 times when steam distillation is used.

shale oil may be made to yield a much larger proportion of spirit than that normally available from it.

The most important step in the development of American oil shale so far (Feb. 1, 1919) recorded, according to **H. J. Wolf,**[1] is being taken by the Ute Oil Co., of St. Louis, Mo. This company is erecting a 400-ton shale oil plant about eight miles from Watson, Utah, on the White River. This is the largest shale-retorting plant under construction in this country. The **Wallace** process is to be used. The decision to erect the new plant was based on the results of extensive testing of many samples of shale. The site of the new plant was carefully considered with regard to the availability and the delivery of the shale, and the disposal of the residue. The deposit is in the form of a long, high bluff, with no overburden.

Methods of Mining and Milling [2]

The mining consists of drilling and blasting down a supply of shale once or twice a week. The shale is then broken by hand to 10 by 15-in. size, and delivered to a 48-in. American pulverizer of ring-and-hammer type, capable of receiving a piece as large as 15 by 45 in., and crushing to $\frac{1}{2}$ in., with 20 per cent fines and 10 per cent over $\frac{1}{2}$ in., with a capacity of 50 tons per hour. The crushed material will be delivered, by an endless belt conveyor, to shale storage bins. From the bins the material will be received by larries, three in number, running on separate monorails. Each larry will serve six retorts. The oil from the retorts will be conducted through condensers and washers into a large crude-oil storage tank. Each retort holds one ton of shale. It is claimed that the process will extract 90 per cent of the total available oil in one hour. Shale from this locality yields an average of 54 gallons of oil per ton of shale retorted. The lowest yield is 31.5 gallons and the highest is 80.5 gallons per ton. It is estimated that the shale, retorted, will yield about one barrel of oil per ton.

In the state of Colorado oil-shale retorting plants have been installed or are in process of erection, in the vicinity of De Beque. The American Shale Refining Co. is developing oil-shale properties on Conn Creek, about 12 miles from De Beque. This company plans to install several 150-ton **Wingett** retorts. One of these retorts has been made by the McFarlan-Eggers Machinery Company of Denver, and has been shipped to the property. A 3000-ft. tramway, with a capacity of 900 tons per day, is to be installed to deliver shale from the mine to

[1] Eng. and Min. Journal, 1919 (107), 217.   [2] **Wolf,** *loc. cit.*

the retorting plane. The company's property has an area of 12,000 acres. The shale cliffs rise to a height of 2500 feet. There are five different strata of oil shale. The highest and richest stratum is 60 feet thick. Extensive tests indicate a yield of 60 gallons of crude oil per ton. A second stratum 200 feet below the first is 75 feet thick and is expected to yield 50 gallons per ton. The available oil in these two strata is estimated at about 20,000,000 bbl., and the ammonium sulphate at approximately 20,000 tons.

The Oil Shale Mining Company is developing property on Dry Creek, twenty miles northwest of De Beque. It has erected six retorts of the Henderson type, each with a daily capacity of 6 tons. This is the first plant of its kind in the United States. The seam of oil shale is 10 to 20 feet thick, and averages 75 gallons of oil per ton. The Mount Logan Oil Shale Mining and Refining Company is developing property on Mount Logan, four miles from De Beque. It has three 20-ton retorts. Samples of shale have yielded as high as 100 gallons of oil per ton. The Colorado Carbon Company is developing property on Kimball Creek, twenty-seven miles from De Beque. Its main seam of shale is 60 feet thick. Samples indicate a yield of 70 gallons of oil per ton. Many small companies have been formed with the view of exploiting oil-shale deposits in a limited way, but most of these organizations are not supplied with adequate capital for the work they have undertaken.

R. W. Lesley[1] proposes to make recovery of ammonia and oil from low-grade carboniferous material such as shale, low-grade bituminous coal, lignite and the like, an integral part of Portland cement manufacture. The method proposed for accomplishing this consists in utilizing the waste heat in flue gases from cement rotary kilns to distill oil from the low-grade carboniferous material. The residue from the destructive distillation of the latter consisting of argillaceous material containing fixed carbon is discharged from retorts and conveyed to rotary kilns after being mixed with calcareous material for the production of cement. If for example shale is the material employed, hot spent shale from retorts containing a certain proportion of fixed carbon is mixed with limestone and used as raw material for the manufacture of cement in rotary kilns working in conjunction with shale retorts.

The fixed carbon in the shale is burned during the process of cement clinkering and its fuel value utilized in this way. Ammonia may also be recovered simultaneously from nitrogen contained in the spent shale. In addition to utilizing the fuel value contained in fixed carbon present in the spent shale, the permanent gases from the shale retorts are also employed to assist in the cement burning.

[1] U. S. Patent 1,323,294, Dec. 2, 1919

The process is said to be applicable to many varieties of low-grade carboniferous material, including the waste piles from the washeries of many of the bituminous coal mines.

Tentative figures have been made [1] on a cement plant producing Portland cement in the ordinary way as against the plant employing
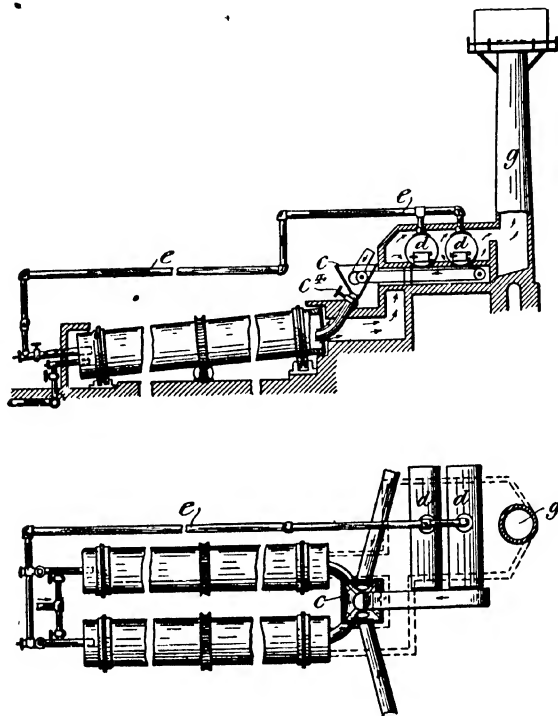
Fig. 206. — Diagram of Leslie process for distilling shale and utilizing spent shale.[2]

the Lesley process.   For a plant located at a coal or shale mine, using the round figures of 125 tons a day for the kiln as against 375 tons of shale, it is figured that there is an increased gain of 62 cents (per barrel of cement produced) from the Lesley process as against a plant similarly located using the ordinary cement clinkering process.

Figure 206 shows an outline of a process.   Retorts for distilling the low-grade carboniferous material are indicated at d and are heated by

[1] Chemical Age, June, 1920, p. 207.

[2] Cut furnished through the courtesy of Lloyd Lamborn, Editor of Chemical Age (N.Y.).

the flue gases from the rotary cement kilns. A conveyor located in front and immediately beneath the retorts conveys hot spent shale to a hopper c, which discharges the material into the rotary kiln. Fuel gases are removed from the shale retorts and conveyed by the pipe e to the front ends of the kilns. A stack g represents an ammonia recovery unit.

Some of the possibilities of the oil-shale industry have been optimistically delineated by **H. M. Roeschlaub**.[1] He calls attention to the enormous shale beds of Colorado, Wyoming, Utah, and Nevada, deposits capable of yielding 42 gallons of oil per ton and the Colorado beds having a thickness which would give 110,000 tons per acre. Phosphates, gilsonite and small amounts of elaterite are associated with the shales. The temperature required varies with the different shales, but ranges from 150° to 700° F. (66° to 360° C.). Oil recovery should be the primary object, while permanent gases and ammonia compounds should be secondary products. A continuous retorting process with stirring devices is needed, in order to prevent matting or fusion of the shale. As each ton of American shale will produce 2500–3500 cu. ft. of fixed gas (in addition to oil vapors) with a fuel value of 450 B.T.U. per cubic foot, and as 350,000 to 500,000 B.T.U. are required to retort one ton of shale, an efficiency of only 50 per cent should give sufficient gas for oil recovery, with an excess to generate steam for operating purposes. Mining and crushing will present no specially difficult problems. It is probable that up to temperatures of 600° F. (371° C.), 10 pounds of ammonium sulphate per ton will be produced, but a larger production of ammonia will require higher temperatures and a retort of special and more complicated construction. The shale-oil residuum, after removal of naphthas and light lubricants, is supposedly valuable for flotation purposes. The spent shales contain 0.5 to 6.0 per cent of nitrates and some phosphates, and possibly could be utilized for fertilizer. Roeschlaub regards the time and conditions ripe for a wide exploitation of the Western oil shales.

A. L. Pearse[2] expresses the opinion that owing to the chemical and physical differences in American shales, no single type of retort is adapted for all. The requirements for oil recovery and ammonia production from shale are conflicting; temperatures below 900° F. (482° C.) are best for oil and 900° to 2000° F. (482° to 1093° C.) for ammonia. As Scotch shales are lower in oil yield and higher in nitrogen than Colorado shales, less attention is likely to be given to ammonia in the case of the latter than has been the practice in Scotland. Potash recovery is not

[1] Chem. Abs. 1920, 463; Eng. Mining J. (1919) (108), 572–6.

[2] Chem. Abs. 1919, 2438.

likely to be of interest in the industry when established. A 1500-ton Scotch type of plant probably could be erected for $2000 per ton day. A figure for a 1000-tons-per-day plant in Colorado has been given as $1200 per ton day. Both plants are of the vertical continuous type. If on a railroad, more modern types presumably could be erected for $800 to $1000 per ton day for capacities above 1000 tons per day. The costs for recovering and refining ammonium sulphate may be figured at $1.25 per ton. Retorting may be figured at $0.70. By adding the cost of mining and the usual general charges, the basal figure for products can be approximated. Air-tight retorts into which steam may be injected Pearse considers to be the only successful types. He thinks that any process involving mass-carbonization (as in coke ovens) is not likely to succeed. The (capital) risk in distilling shale oil is asserted to be less than that in oil-well (petroleum) operations and the cost of obtaining the products from a barrel of shale oil (shale yielding a barrel of shale oil), to be no more than the average cost of a barrel of oil-well products (cf. cost estimates given on page 575).

Shale Distillation in Scotland [1]

Retorting. – Each hopper, which is closed at the top with a lid or cover about eighteen inches in diameter, holds several hours' supply of broken shale. Moist sand is used to make a seal around the rim of the cover. The retorts are vertical and tapered, being about two feet in diameter at the top and three feet at the bottom, and the shale feeds by gravity. The taper aids the free downward movement of the shale. The upper part of the retorts are one-piece iron castings that average about 12 feet high. It is in this part that the bulk of the oil distills. The vapors and permanent gases are removed under slight suction through a pipe that forms a part of the top of the casting. The lower part of the retorts is built of one tier of specially shaped fire brick, and averages about 18 feet high. In this part the shale is brought to its maximum temperature, about 1700° to 1800° F, and most of the ammonia and water gas are formed, through the action of steam on the red-hot carbon and nitrogenous material remaining in the shale. The shale is discharged from the retort into a sealed hopper that holds several hours' output of spent shale. Differences in the mechanical devices for continuously discharging the spent shale are important features that distinguish the different types of these retorts. Exhaust steam, about 750 to 1000 pounds of steam to 2240 pounds of shale, is admitted into the hopper holding the hot spent shale. This steam serves many purposes; (1) to cool the shale in the bottom of the retort, (2) to carry heat from the spent shale into the retort, (3) to form water gas from the fixed carbon, (4) to form ammonia by reacting with the nitrogen in the shale, (5) to sweep the oil vapors out of the retort, and (6) to effect a better transfer of heat from the walls of the retort to the center of the charge.

Four retorts are usually set together in a common furnace, and sixteen of these units of four constitute a bench, which is two retorts wide and thirty-two long. The retorts are heated by permanent gases resulting from the destructive distilla-

[1] U. S. Bureau of Mines, notes on Oil Shale Industry, May 1, 1919.

tion of the shales. Experience in Scotland has shown that a Scotch shale yielding 25 imperial gallons (27 U. S. gallons) per short ton or more of oil per long ton of shale, will also yield enough fixed gases to heat the retorts. When the permanent gases from the retorts are insufficient for heating, producer gas is manufactured and used. The average capacity per day at the present time in Scotland is about four long tons (four and one-half short tons) per retort. In Scotland, no use has ever been found, it is said, for the spent shale, and it receives no treatment after being discharged from the hoppers under the retorts, but is dumped in huge heaps, called spent-shale bings. The disposal of these great quantities of spent shale presents considerable practical difficulties and items of expense connected with the industry.

Separation of Products. — The oil vapors, gases and steam from the retort pass into a common header and then through air-cooled, vertical condensers. The oil and water vapors from the condensers run into separators, where the oil is separated from the ammonia water. The non-condensible gases are passed through scrubbers in order to remove the light oils and ammonia and are then used as fuel for heating the retorts. This gas with the gases from the oil stills constitutes a large percentage of the total fuel used at the plant. After being separated from the ammonia water, the crude shale oil is transferred to the crude stills, where it is separated into various fractions by distillation. The scrubber oils are also distilled and the light oils thus obtained are added to the corresponding products from the distillation of the crude shale oil.

The refining of shale oil is much like that of petroleum, although the operations are more complex and more expensive. Shale oil differs from crude petroleum in containing certain organic compounds that have a particularly bad odor and must be removed before the product is marketable. Also, shale oil is more highly unsaturated than petroleum and hence requires more careful refining. The removal of unsaturated products and compounds having a bad odor necessitates several distillations and acid and alkali treatments, which increase the refining costs and losses. The average refining loss for shale oil in Scotland is about 25 per cent, as compared to about 7 per cent in completely refining petroleum. The ammonia water obtained from the scrubber and separators is distilled and the ammonia obtained is passed into sulphuric acid to form ammonium sulphate.

Yield of Products. — The shale now being retorted in Scotland yields on the average about 24.5 U. S. gallons of crude oil and about 35.7 pounds of ammonium sulphate per short ton. The yield of gas per short ton of shale retorted varies somewhat, but on the average is about 9800 cubic feet; its heating value is about 240 B.T.U. per cubic foot.

The products obtained by refining the crude shale oil are as follows: motor spirit, illuminating oils, gas and fuel oils, lubricating oils, paraffin wax and coke. The yield of these different products varies and depends to a certain degree both on the nature of the shale and on the conditions of retorting and refining. As a rule, three grades of lubricating oil are made, none of which is suitable for steam cylinders, internal combustion engines or heavy duty bearings.

The following account is given of refinery operations in Scotland as described by **Steuart** [1] where, of course, the industry has been on a much more stable and commercial basis than it is in America. However,

[1] *Loc. cit.* pp. 179–194.

according to recent advices [1] it is reported that the refining of oil from shale in Scotland is no longer profitable and that the plants will be used for the refining of Persian petroleum.

The Refinery. — The refinery consists essentially of (1) stills for the repeated distillation of the oil; (2) stirring-tanks, in one set of which the oils are treated with strong sulphuric acid, and in another with caustic soda; (3) paraffin-houses, in which the heavy oil containing the solid paraffin is cooled and pressed, and where there are great refrigerating machines; (4) paraffin refinery; (5) stock tanks for the finished product; (6) filling shed with cooperage, where the products are filled into barrels and tanks to send to the customers; and sometimes (7) a candle-house to make the solid paraffin into candles; and occasionally (8) vitriol chambers to make the sulphuric acid required, and concentrating plant.

The crude oil is settled from the ammonia water and shale-dust, and pumped up into a high charging tank, from which the oil can flow by gravitation into the stills. There are heat interchangers on the top of the stills, so that the cold oil-feed flowing in is heated by the vapors distilling out. There are high charging tanks behind each bench of stills and low tanks to receive the distillates. With every distillation, steam, more or less superheated, is introduced into the stills; hence there are steam boilers at hand. Water converted into steam expands about 1700 times. Shale oils expand only one or two hundred times, and when distilled without steam a great deal of oil has to be evaporated before the vapors mount up to the exit pipe. Their specific heat and heat of vaporization are not great, and they readily condense on the top of the still to fall back and be redistilled with some decomposition. When steam is introduced it supposedly cushions and protects the gaseous molecules from decomposition, and rapidly sweeps them into the condenser. Further, the presence of steam lowers the boiling point of the oil in much the same way as a vacuum or reduced pressure.

Refinery Operations [2]

Distillations and Chemical Treatments. — The crude oil distillation is meant to be a destructive one to some extent, and the steam admitted is limited. If the crude oil be treated directly with oil of vitriol and caustic soda the loss is very great. Or if too much steam is used in the distillation the loss with the treatments is great, as the steam drives the oil over unchanged. The distillation apparently converts tarry or resin-

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[1] J. Ind. Eng. Chem. 1919, 1098, Commerce Reports 1919 (Aug.), p. 937.
[2] Steuart, *ibid.*

ous matters capable of uniting with the refining chemicals, into the required hydrocarbons. Steam is limited in amount when near the end of the second distillation also; but when the bulk of the heavy oil and paraffin is passing over, the proportion of steam is high.

The once-distilled oil is stirred up with oil of vitriol and the black viscous tar settled out. The oil is run into another tank, where it is treated with caustic soda, and here another black viscous tar is separated. The settled oil is pumped up to the charging tank of the next distillation. The stirring during chemical treatment is sometimes done with mechanical stirrers, but more often with air, pumped into the bottom of the tanks.

At each distillation a fractionation is made, that is to say, the oil is separated into naphthas, burning oils, and heavy oils. In the crude distillation sometimes only the naphtha or spirit is separated and all the rest distilled together as "green oil." The burning oil is left with the heavy oil and paraffin so as to keep the mixture liquid at a comparatively low temperature for the acid treatment, otherwise a high temperature would be required, and this would cause the acid to attack the olefins. The amount of oil of vitriol used is limited for the same reason, as well as for economy.

After the first treatment with oil of vitriol and soda, the next distillation separates burning oils of various gravities and the heavy oil containing paraffin. The burning oils are distilled again, sometimes repeatedly. The oils vary in specific gravity in different works, and at different times in the same works, to suit the requirements of the market.

Separation of the Solid Paraffin.--The heavy oil is cooled in shallow tanks set in sheds open to the wind, and afterwards with freezing machines. The old cooling drums, dipping into the oil and paraffin and raising a film to be scraped off at the other side, are no longer used, as they chill the mixture too rapidly and prevent proper crystallizing of the solid. Ammonia machines are now always used, some beginning with ammonia solution, and others with dry gas liquefied by pressure. The ammonia solution machines cool a solution of chloride of calcium which cannot be frozen by the machine, and this chilled brine is put into a tank filled with alternate compartments; wider ones for the oil and paraffin and narrower ones for the brine. The oil and paraffin lie there for hours exposed to the cold, and the solid paraffin separates out in good crystals. In the Beilby cooler, the paraffin mass lies undisturbed until chilled to the extent required. In the Henderson cooler, a scraper goes slowly round, removing the chilled mass from the cold plate and letting the warmer material forward to the cold. Paraffin

is a bad conductor of heat, and, in the Beilby cooler, the paraffin mixture requires to lie a long time and necessitates a large plant, but gives a better crystal. In the Henderson cooler much more can be put through and yet a sufficiently good crystal is obtained.

The heavy oil separated from the solid paraffin is called " blue oil," which is treated with oil of vitriol and soda, and is distilled again and separated into the various fractions according to the gravity required. These, after cooling and pressing from soft paraffin, and when further treated with oil of vitriol and carbonate of soda, are ready for the market. If the solid paraffin is thoroughly separated from the lubricating oil, the latter becomes proportionately heavier in gravity and more viscous, and the setting point is lowered. The solid paraffins are refined by a sweating process. The sweatings are run into receivers according to melting point and color.

The Stills. – In the distillations the bulk of the oil is distilled off from boiler-stills, which are horizontal cylinders, the charge being two or three thousand gallons, and the residue is run into round cast-iron-bottomed stills to be distilled to dryness and coked. The still coke of the crude oil is valuable. When the coking is in progress, much permanent gas is given off, very pure, of high luminosity, and valuable for lighting or fuel. These gases used to be passed into the atmosphere and lost; now they are all carefully utilized after scrubbing light spirit from them.

N. M. Henderson connects boiler-stills into a series, the oil flowing from one to another, and each giving off a distillate of a fixed specific gravity. They are worked continuously, save when temporarily stopped for cleaning operations. At the end of the series is a residue still with cast-iron bottom, which, when charged, is disconnected and another residue still is put on to the series. By this method twice as much oil is put through as when the stills are separate, and the distillation is more perfect and requires less oversight.

In a crude oil distillation by the old method, naphtha passed over first, and was run into its own tank. At a certain specific gravity the distillate was run into another tank. The temperature in the still gradually rose, together with the specific gravity of the distillate, the latter giving in succession burning oil, intermediate oil, heavy oil with paraffin, and at the end, still grease. The specific gravity had to be constantly tested to fix when the materials should be turned into another tank. With the connected stills, the first always discharges naphtha, the second burning oil, the third intermediate oil, and the fourth heavy oil and paraffin. There is considerable power of adjustment to suit what is required.

In the manipulation with oil of vitriol, the tar from the finishing treatment is used to give a first treatment to the crude oil distillate. The tar from this oil is washed with hot water to separate the sulphuric acid, which is sent to the ammonia house, and the tar, neutralized with soda tar, is settled and burned as liquid fuel under the stills, being blown into spray with superheated steam. It burns like a jet of gas, with smokeless flame, and the chimney gases are said to have no more sulphur than from coal.

Quantities of Chemicals Used. — To the crude oil distillate is added acid, equivalent to more than 2 per cent of oil of vitriol, the after treatments of the light oil ¼ per cent, and the finishing treatment of burning oil 1 to 2 per cent, according to previous treatment, etc. The blue oil receives about 1 per cent of oil of vitriol and a finishing treatment after fractionation from 2 to about 4 per cent oil of vitriol. The caustic soda treatments are about 1 per cent of solution of 60° Tw., or 1.3 sp. gr., except in the finishing treatment, when the burning oils receive very weak caustic soda, and the lubricating oils carbonate of soda solution.

Blue oil is treated with dry caustic soda in a still, from 2 to 5 lbs. to 100 gallons.

On the following page is a scheme of refinery operations. O.V. means Oil of Vitriol, and C.S. Caustic Soda.[1]

The crude oil obtained from shale is reported to be substantially a mixture of hydrocarbons of the paraffin and olefin series, with a small admixture of naphthenes and aromatics. Members of both the paraffin and olefin series occur in the naphthas and burning oils.

The members of the olefin series have a higher specific gravity than those of the paraffin series, and the series with still less hydrogen than the olefins possess an even higher specific gravity. These last are removed by sulphuric acid, which reduces the specific gravity of the oil remaining. The more unsaturated hydrocarbons and the sulphur compounds have an odor like garlic. A trace of these gives the penetrating smell to paraffin oil, and its removal, without destroying any of the useful products, is the problem of the refiner.

The sulphuric acid used in refining combines with pyridine bases and other basic substances, the bulk of the phenols, the sulphur compounds, and highly unsaturated hydrocarbons. The caustic soda solution extracts phenols and acids. In the finishing treatments an effort is made to extract the last traces of the compounds more unsaturated than olefins, and also the sulphur compounds. Compounds are then formed which give a white emulsion with soda solution. Any trace of the soda sulpho-compound left in the burning oil causes a crust in the wick of the lamp, and care has to be taken to wash thoroughly.

[1] Steuart, *loc. cit.* p. 188.

DIAGRAM SHOWING PROCESSES OF MANUFACTURE (SCOTCH SHALE OIL)

Crude Oil
distilled.

Naphtha,
O. V. and C. S.
distilled

Naphtha, 0.730

Naphtha, 0.740

Residue of Light Oil.

Green Oil,
O. V. and C. S.
distilled.

Still Coke.

Light Oil.
O. V. and C.S.

Heavy Burning Oil.
O. V. and C. S.
distilled.

Heavy Oil and Paraffin.

Coke

Burning Oil.
O. V. and C.S.

Gas Oil,
Cooled and Pressed.

Heavy Oil and Paraffin.

Soft Paraffin.

Gas Oil, 0.850.

Distilled.

Cooled and Pressed.

Hard Paraffin Scale,
sweated.

Naphtha   Burning Oil,   0.785.   Burning Oil, 0.800.   Burning Oil, 0. 810.   Gas Oil.

Blue Oil,
O. V. and C. S.
distilled from C. S.

Lub. Oil,
Cooled and Pressed.

Soft Paraffin.

Sweatings,
re-sweated.

Wax,
re-sweated.

Lub. Oil.
Cooled and Pressed.

Lub. Oil 0.865   Soft Paraffin.

Lub. Oil 0.885.   Soft Paraffin.

Match Wax,
100° M. pt.

Paraffin Wax,
110° M. pt.

Paraffin Wax,
115° M. pt.

Hard Wax

. The Composition and Properties of the Products of Manufacture

1. *The Permanent Gases of the Retorts.* — These are used for fuel. The composition varies with the state of the retort at the time and with other circumstances. Excess of nitrogen indicates, that air has been sucked in by the action of the exhauster.

	Young & Beilby Retort Hermand Type (Foster)	Henderson's 1873 Retort	Henderson's New Retort, 1901	Bryson Retort (Bryson)
Carbon dioxide and hydrogen sulphide.....	20 7	18 0	26 0	22 08
Olefins	1 6	5 0	1 2	1 38
Oxygen	3.6	2 0	1 0	1 18
Carbonic Oxide, CO	1 16	0 0[1]	7 8	9 77
Marsh-gas	8 66	38 4	9 2	3 70
Hydrogen . .	21 68	28 7	38 6	55 56
Nitrogen .	42 6	7 9	16 2	6 33
	100 0	100 0	100 0	100 00

2. *Shale Naphthas* are thin, limpid, mobile, colorless liquids, completely volatile at ordinary temperatures. They generally consist approximately of 60 to 70 per cent of olefins and other hydrocarbons acted on by fuming nitric or sulphuric acid, the rest being principally of the paraffin series.

Broxburn Naphtha, sp. gr. 0.735, after repeated fractional distillations and treatment with sulphuric acid and soda solution gave the following results:

	Range of Temperature	Volumes	Loss by Treatment, Volumes	Paraffins, Per cent	Olefins, etc.
1.	26 to 37° C	4,000	2,800	30	70
2.	37 " 45 " ...	5,000	3,200	36	64
3	45 " 58 " ..	2,275	1,225	46	54
4.	58 " 65 " ...	9,300	5,125	45	55
5.	65 " 67 " ..	4,900	2,600	47	53
6.	67 " 69 "	14,200	7,200	50	50
7.	69 " 72 "	10,110	5,160	49	51

[1] Steuart, *ibid*, p. 189.

In the oil from the Henderson 1873 retort, there was often no benzene, but in the oil from the existing retorts the benzene series is distinctly represented. In Broxburn Naphtha, sp. gr. 0.735, the fractions boiling between 55° and 75° C. gave 2.6 per cent benzene, and the fraction 100° to 105° C. gave 2.5 per cent toluene. The members of this series were found to distill at temperatures under their true boiling points. And, where they were expected, fractions sometimes showed no trace of them. The naphthenes methyl-tetramethylene, pentamethylene, and hexamethylene were present in distinct quantities.[1].

Friedrich Heusler has examined the fraction of Scottish paraffin oil boiling below 110° C. (naphtha or spirit), and found paraffins 42 per cent; naphthenes 10 per cent; aromatic hydrocarbons 7.3 per cent; olefins 39 per cent. He proved the presence of benzene, toluene, metaxylene, and cumene, and the absence of naphthalene. The corresponding figures he obtained for Saxon lignite — of vegetable origin — were: - paraffins 16, naphthenes 4, aromatic hydrocarbons 45, and olefins 31 per cent. •

3. *The burning or lamp oils* are transparent, nearly colorless, thin liquids, having both the paraffin and olefin series in large proportion. There are 30 to 40 per cent of unsaturated hydrocarbons that can be taken out with fuming sulphuric acid.

4. *The lubricating oils* are transparent, yellow-colored, bright liquids with considerable viscosity. For oils from the same source, the viscosity varies with the specific gravity; but for oils from different sources the specific gravity is no measure for the viscosity, as the lower gravity of oil may have the higher viscosity. They are to a large extent olefins, but mixed with liquid paraffins.

5. *The solid paraffins* are colorless, tasteless, odorless bodies, composed of saturated hydrocarbons. They are able to resist the action of the strongest chemicals, which makes them useful for many purposes. They are good insulators. They are somewhat plastic for a good many degrees below their melting points, and hence low melting point candles sometimes bend with their own weight in hot weather. The flashing point of wax of m. pt. 128° F. (53° C.) is 375° F. (190° C.). Heated in a bath in air the vapors do not ignite spontaneously at 620° F. (327° C).   •

The following table gives the properties of average samples of the usual products:

[1] B. Steuart, *Jour. Soc. Chem. Ind.* XIX, p. 986.

	Sp. Gr.	Flash Point Range		Tint, No 500 glass Lovibond, 2-inch Cell	Boiling Point Range		Viscosity by a certain Pipette
Motor Spirit	.715	Lowest Temperatures		Colorless	120° F –300° F.		..
Spirit of Naphtha . .	.735			"	140 " 320 "		..
" "	.740			"	180 " 380 "		..
Special Oil, or Water-white Oil .	785	106° F.–120° F		..	310 " 500 "		..
Crystal Oil....	800	115 " 125 "		0 5	340 " 575 "		..
No. 1 Burning Oil	805	110 " 135 "		0 75	310 " 580 "		..
Lighthouse Oil	810	145 " 160 "		1 0	390 " 573 "		..
Mineral or Marine Sperm . .	830	200 " 230 "		2 0	450 " 675 "		..
Mineral Colza	840	220 " 240 "		5	500 " 700 "		..
Gas Oil	855	200 " 230 "		..	450 " 710 "		..
Gas Oil, Grease Oil, Cleaning Oil	870	275 " 300 "		.	500 " 720 "		..
Lubricating Oil. . . .	865	275 " 300 "		15	575 " 710 "		44 seconds
" "	.875	300 " 310 "		18	575 " 800 "		47 "
				½-inch Cell			
" "	885	320 " 310 "		15	650 " 870 "		55 "
" "	890	330 " 350 "		16.	720 " 875 "		70 "

In determining the flashing point the Abel apparatus is used; the whole apparatus for the lower flashing burning oils, and the cup of it for heavy oils. The tint is taken by different methods. The method of taking the boiling range most recognized is that of Engler. The viscosity or body is generally taken with a pipette, each company having its own standard tube. There are viscosimeters by Redwood and by Engler that are used as standards of reference.

The boiling range of oils is set forth in the annexed table:

	Lub Oil 890/5		Lub Oil 885/90		Lub. Oil 865		Oil 810		Oil 830	
	Temp	Sp Gr	Temp	Sp Gr	Temp	Sp Gr	Temp	Sp Gr	Temp	Sp Gr.
First drop over	725° F	.	675° F	.	575° F	.	450° F		500° F	
1st 10 per cent over	745 '	886	705 "	878	600 "	856	500 "	806	510 "	818
2nd 10 " "	745 "	888	715 "	880	605 "	857	530 "	823	515 "	821
3rd 10 " "	750 "	889	720 "	882	610 "	858	545 "	829	520 "	.824
4th 10 " "	760 "	891	730 "	884	615 "	860	560 "	836	530 "	.826
5th 10 " "	770 "	895	740 "	887	620 "	861	570 "	839	540 "	829
6th 10 " "	780 "	898	755 "	890	630 "	863	585 "	813	550 "	830
7th 10 " "	790 "	901	775 "	893	635 "	864	605 "	817	565 "	831
8th 10 " "	805 "	904	795 "	898	650 "	868	630 "	852	585 "	832
9th 10 " "	820 "	907	830 "	904	670 "	872	660 "	856	615 "	834
(95 " "	830 "	.	840 "	..	680 "	..	675 "	..	630 "	..
(97.5 " "	850 "	..	850 "	..	695 "	..	690 "	..	645 "	..
10th 10 " "	875 "	919	880 "	912	710 "	879	700 "	.863	675 "	.841

Ten thousand fluid grains were distilled from a copper flask, and the distillate was collected in 10 per cent fractions and the sp. gr. of each fraction taken.

The Uses of the Products of Manufacture

Naphtha, or spirit, completely volatile at ordinary temperatures, possesses different specific gravities and boiling points according to requirements — 0 660 for gasoline, for instance, and 0.700 to 0.720 for motor spirit Ordinary naphthas, 0 725 to 0.745, are largely used for lighting purposes in special lamps in workshops, shipbuilding yards, etc.; and, for solvent purposes, in dissolving india-rubber, for water-proofing, and removing grease from clothes, for dissolving gums and resins, wool-washing, paint-mixing, in the preparation of varnishes and of alkaloids, extraction of oils and fats, in linoleum making, and largely also for refining paraffin wax. It has been employed for freezing machines, and also as a local anaesthetic.

Burning oils are used for lamps of many forms, sp. gr. varying from 0.785 to 0 830, and flashing point from 105° F. (40° C.) to 230° F. (110° C.). Scottish oils have been free from lamp-accident fatalities since their manufacture over sixty years ago. The special, or water-white oil (sp. gr. 0 785), is serviceable for continuous burning lamps for buoys, lightships, etc., which can be retrimmed only at long intervals, from a week to a month. These burning oils are also utilized for combustion in oil engines. Lighthouse oil is specially safe for light-houses Marine sperm is employed on board ships, with lamps slightly modified to suit the heavier oil, and it does not give off vapor that can ignite until much above the boiling point of water. Mineral colza (sp. gr. 0 840) is used also with special lamps.

Intermediate oils (sp. gr. 0 840 to 0 870) are used for gas making. They are very pure, require no refining for the gas, and are employed where gas lime is objectionable. They produce gas of high illuminating power, and they are largely used for enriching coal or water gas. Oil-gas, compressed, is used for lighting railway carriages. Safe itself under pressure, it has also the power of rendering acetylene safe Acetylene is very rich in light-giving power, but is by itself explosive, so that it may not be stored under greater pressure than 3 6 lbs. per square inch. If one part of acetylene be mixed with four parts of oil-gas, the Home Office Regulations allow pressures up to 150 lbs. per square inch. Intermediate oils are employed for combustion in oil engines. Considerable quantities reported to be used as fuel by the British Navy.

Mineral oils of all kinds, but chiefly the intermediate oils, are used for cleaning purposes, for removing rust from iron, and gummy matter which collects on machinery bearings when vegetable or animal oils are used as lubricants, etc Intermediate oils are also employed for grease making. In the tropics heavy mineral oils are effective for protecting wood work from the white ants (termites).

Lubricating oils are made with sp. gr. varying from 0 865 to 0 910, and are used either alone or mixed with vegetable or animal oil. Mineral oil prevents vegetable or animal oil from undergoing spontaneous combustion on cotton waste, etc, and thus greatly increases the safety of these fatty oils for employment in mills (Galletly). Shale lubricating oils do not decrease so rapidly in viscosity by heating as some other mineral lubricating oils. Some companies produce cylinder oils.

Still grease is the amorphous distillate from the end of the crude oil or heavy oil distillations, and is employed for grease making.

Still coke, which is the residue left in the still on distilling crude oil to dryness, is used as a fuel.

The costs of refining shale oil in Scotland, given herewith,[1] are for the year 1919 and are not necessarily applicable to American conditions and American shale oils. Refining crude shale oil in one of the largest works in Scotland, manufacturing the following products, exclusive of plant depreciation and packing and shipment of products, costs approximately $1.05 per barrel of 42 U. S. gallons.

Products made are:

Naphtha (including scrubber naphtha) .   ..   9 9 % (450° F. end point)
Burning oil   . .   .   .   24 7 %
Gas and Fuel Oil   .   ...   24.4 %
Lubricating Oil   .   ...   6 6 %
Wax   ....   9 5 %
Loss (including still coke 2 %) ....   24 9 %
                                     100.0 %

Attention is called to the high refining loss and to the fact that the lubricating oils, by reason of their low viscosity, command a considerably lower price than lubricants made from petroleum.

Morrell and **Egloff** [2] have determined that the percentage of unsaturated bodies in the distillation fractions of shale oil showed two maxima and one minimum. The first 10 per cent contained 32 per cent, the 20–30 per cent fraction 24 per cent, and the 80–90 per cent fraction the high value of 50 per cent unsaturated. Small percentages of benzene, toluene and xylene were found in the oils examined. Phenol, o- and m-cresol, xylenols and guaiacol comprise the list of phenols so far identified in shale oil. Pyrrole, pyridine, picoline, lutidine and parvoline have been identified also. The shale-oil industry of France and that of New South Wales have, it is said, declined or failed to advance. The average yield of oil from United States shales is stated to be about 20 gallons per ton. The naphtha fraction of nine samples was found to be 10 per cent. This product is reported to be unsuitable for use in gasoline engines and cannot be refined by the usual sulphuric acid-caustic soda process. It is contended that Scotland has averaged less than 1 per cent marketable gasoline from her shale oil during the last fifty years. It is also maintained that United States shale oil will certainly yield very much less than 10 per cent marketable gasoline. Morrell and Egloff are convinced that oil shales will be of great

[1] U. S. Bureau of Mines, Notes on Oil Shale Industry, May 1, 1919.
[2] Chem. Abs. 1918, 1924; Chem. Met. Eng. (1918) 19, 90–6.

economic importance in years to come but express the belief that, (1918) the problems of the future industry are largely unsolved.

This discussion does not appear to take into consideration the possibilities of blending shale naphtha with "straight distilled" petroleum naphtha, or with benzol and alcohol, or with casing head or natural gas naphtha so as to reduce the per cent of unsaturated material to a suitable degree.   (Authors.)

Roy Cross [1] holds the opinion that shale oil will not make a satisfactory gasoline without excessive refining losses, and that it is commercially adapted for fuel and illuminating purposes only. The only successful shale operations, it is said, are now in Scotland, where less than two million barrels of shale oil were produced in 1916 by six companies. Cross' observations indicate that average good shale which will be available in Colorado will yield 54 gallons of oil per ton, which he believes alone will not be profitable, but a ton of shale will also yield 34 pounds of $(NH_4)_2SO_4$, which will make the industry attractive. There may be expected, it is said, from the commercial exploitation of Colorado shale, the following:

Proceeds per ton		1918	1913
54 gal. oil (405 lb)	....	$2 70	$1.00
34 lb. $(NH_4)_2SO_4$	....	2 46	1 09
		$5 16	$2.09

Costs per ton are calculated to be $4.34 for 1918 and $3.16 for 1913. It is maintained by Cross that there is little prospect that shale oil will replace petroleum in the near future for any uses but as fuel.

E. W. Thurlow [2] proposes obtaining motor fuel from shale by mixing the latter in the form of powder into material which yields carbon dioxide when heated, such as limestone, dolomite, carbonate of magnesium, or barium carbonate, together with finely divided iron and subjecting the whole to destructive distillation in a retort at temperatures ranging up to 800° C. (1472° F.) until the evolution of vapors ceases. The temperature is then increased beyond 800° C. (1472° F.) and water in the form of a fine mist or jet is injected into the lower part of the retort. The finely divided metal is intended to react with the steam for the production of hydrogen during the initial or destructive distillation; the evolution of carbon dioxide according to Thurlow assists in removing condensible hydrocarbons from the zone of decomposition.

Van H. Manning has recently pointed out that a large part of our native oil supply remains associated with oil sands and is not brought to the surface. Consequently according to Manning a problem which

[1] Chem. Abs. 1918, 762; Nat. Pet. News, 1918, 10, Jan. 16, 42–46.
[2] U. S. Patent 1,343,100, June 8, 1920.

demands serious attention is the recovery of the oil which is held by
the oil sands.

Navin [1] proposes to extract oil from oil sands or shale by agitating
these materials in a finely divided state with a mixture or emulsion of
solvent oil, as for example gasoline, kerosene and the like, and water.
Although this process might be applicable to oil sands, it is difficult
to see how it could be applied to the extracting of oil from shale in com-
mercial quantities since, as is well known, shale will yield only an
extremely small quantity of oil even when extracted with such a powerful
solvent as carbon bisulphide.

W. Forbes-Leslie [2] discusses the geographical, geological, and historical de-
tails of the English shale fields, and states that in the lower layers of the Nor-
folk shale the presence of resinous substances can be detected by the microscope.
When crushed to 30-mesh size the specific gravity of the Norfolk shale is 1.55.
When shaken with ether the shale yields one per cent of oil; carbon bisulphide
extracts only 0.25 per cent. The oil also exudes when the shale is wet. In three
specimens the volatile organic matter varied from 31.7 to 35.1 per cent, the ash
from 39.8 to 46.8 and the moisture from 4 per cent to 10 per cent. The inorganic
matter has also been determined in both the original and the spent shale. The
sulphur content varies from 4.3 to 7.8 per cent and much of this remains in the
spent shale. The yellowish-black mobile oil has specific gravity 0.942 to 0.960.
The yield is 40 gallons to the ton, together with 66 pounds of ammonium sulphate
and 25,000 cubic feet of dry gas. The oil yields a considerable quantity of motor
spirit, 3 to 4 per cent of phenols, and a similar amount of benzene and toluene.
A large proportion of the oil distills from the shale below 300° C. (572° F.). Labo-
ratory experiments show that the sulphur in the oil can be reduced to below 3 per
cent while it seems that some oils containing as much as 4 per cent of sulphur can
be used in internal combustion engines. Calculations based on the extent and
thickness of the Dorset and Norfolk shale beds indicate very considerable additions
to the oil resources of the United Kingdom.

In Germany, prior to the outbreak of war, shale was worked in the
Rhine provinces and near Reutlingen, but only one company was oc-
cupied in producing paraffin and mineral oils. From the bituminous
shale which occurs near Messel (yielding 40 to 45 per cent water, 6 to
10 per cent tar, and 40 to 50 per cent residues) the following yields per
ton of shale are obtained: 135 liters of crude oil, together with 295
liters of ammonia water and 59 cubic meters gas, which is burnt as fuel
in gas engines or under the vertical retorts which are employed. During
the war oil-shale deposits in South and North Germany have been
investigated in regard to their yield, but the results have not yet been
published. [3]

[1] U. S. Patent 1 312,266, August 5, 1919.
[2] J. S. C. I. 1917, 204; J. Inst. Petrol. Tech. 1916, 3, 3–35.
[3] Z. d. Ver. deut. Ingen., July 19, 1919; J. S. C. I. 1919, 378R.

Bituminous shales are found in France near Autun. Detoeuf[1] notes that formerly the distillation was carried on in vertical retorts, 1000 kilograms of shale yielding 50 liters of crude oil and 5 kilograms of ammonium sulphate. The oil is a mixture of hydrocarbons, especially of the ethylene series, some aromatics, chiefly phenol derivatives, sulphur compounds, and paraffin. The Scotch method is now used. Retorts are 15 meters high, of refractory material in the lower part and cast iron in the upper part. They are heated to redness below and to 400° C. above. 135 liters of tarry oil are collected and ·this, on redistillation, yields 65 to 75 per cent crude oil. The gas is washed with heavy oil to remove spirit, and with water to reclaim ammonia not already collected with the tar. It is redistilled and washed successively with sulphuric acid, caustic soda solution and water. The yield on refining is 5 per cent of a spirit of gravity 0.730 to 0.750.

The following list of processes for handling shale[2] is given·

Bishop Process. James A. Bishop, 1526 North Lasalle Street, Chicago, Illinois.

Bronder Process. William F. Mohr, Clark, Long & Company, 50 East Forty-second Street, New York, N. Y.

Catlin Process. R. M. Catlin, Franklin Furnace, N. J.

Chew Process. L. F. Chew, Denver, Colorado.

Crane Process. Crane Shale Corporation, Elko, Nevada.

Day-Reed Process. David T. Day, 713 Nineteenth Street, N. W., Washington, D. C.

Del Monte Process. C. A. Prevost, American Representative, Room 814, Southern Building, Washington, D. C.

Erickson Process. Rainbow Petroleum Products Co , Salt Lake City, Utah.

J. H. Galloupe Process. J. H. Galloupe, 1101 Nineteenth Street, Denver, Colorado

Greene-Laucks Process. F. C. Greene, The Denver Coal By-Products Company, Denver, Colorado.

J. B. Jenson Education Process. C. B. Stewart, 806 McIntyre Building, Salt Lake City, Utah.

Pearse Process. Arthur L. Pearse & Co., 50 East Forty-second St , New York, N. Y.

Pumpherston or "Scotch" Process, Glasgow, Scotland.

Scott Process. Detroit Testing Laboratory, 674 Woodward Ave., Detroit, Mich.

Simpson Process. Louis Simpson, 172 O'Connor Street, Ottawa, Canada.

Stalmann Process. Otto Stalmann, Salt Lake City, Utah, or Petroleum Engineering Co., 217 Dwight Building, Kansas City, Mo.

Wallace Process. George W. Wallace, Consulting Engineer, Wallace Coke, Oil and By-Products Co., East St. Louis, Illinois.

Wingett Process. The American Shale Refining Co., 631 First National Bank Building, Denver, Colorado.

Products and By-Products:

Prichard Process. Dr. Thomas W. Prichard, Chemists' Club, 52 East Forty-first St., New York City.

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[1] Industrie chimique, 1919, 6, 5–7, 35–38; Chem. Abs. 1920, 313.

[2] **Winchester**, Chemical Age, 1919, 121.

CHAPTER XXVII

THE PYROGENETIC TREATMENT OF ASPHALTS

Speaking in a general way, the cracking of asphalts to yield useful distillates holds, with few exceptions, for the purpose of obtaining motor fuel, little economic or technical interest at the present time, at least in this country. The largest deposit of natural asphalt in existence, that at Trinidad, is too valuable as raw material for paving purposes and other industrial uses, in order to be of interest from a pyrogenetic point of view. Moreover it contains finely divided mineral matter or clay, which exists in a colloidal condition in the mass of bitumen.

The Venezuelan deposits contain less clay, but they, too, are of very considerable value, as such, in the many industrial uses which are found for refined and properly manipulated asphalt. The same condition exists with regard to the artificial asphalts produced from reduced asphaltic crude oils.

All of these materials may be made to yield very interesting distillates when distilled destructively, or cracked: distillates which are highly unsaturated, and which may be used for a variety of purposes, e.g., solvent oils and other applications.

Nevertheless, with the past condition of natural resources as regards supplies of petroleum, there has been little need or incentive to turn to asphalts as sources of hydrocarbon oils. Gilsonite stands rather apart from other asphalts in this respect. It has very valuable properties as an asphalt, but the products which it yields on destructive distillation are believed to warrant, for economic reasons, its treatment in this way. It is, therefore, probably the most important asphalt, considered as a commercial source of naphtha and higher boiling oils.

One of the authors of this treatise has devoted considerable attention in the past, to the destructive distillation of asphalts, particularly gilsonite, for the purpose of developing industrial uses for the distillates obtained. The proportion of unsaturated hydrocarbons in distillates from asphalts and pyro-asphalts is generally very much greater than is to be found in crude oil distillates, particularly of the paraffin and semi-paraffin type. The property of asphalt distillates of containing a high percentage of unsaturated hydrocarbons causes them to resemble in this respect the distillates obtained from shale, although it is not

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meant to imply that the raw materials are similar in constitution and composition. It is, however, believed that the large proportion of reactive, unsaturated hydrocarbons in asphalt distillates as well as in shale oil offers very great possibilities for the establishment of a chemical industry, the object of which would be the transformation of the unsaturated hydrocarbons into more valuable products by means of chemical reagents in a manner analogous to the transformation of coal tar distillates.

One advantage which asphalts possess over shale, as sources of liquid and gaseous fuel, is the fact that asphalts in general possess a much higher proportion of oil-yielding material than is the case with shale. Utah gilsonite, for example, is almost pure bitumen, and the residue from its destructive distillation is coke practically free from natural mineral matter. At the present time gasoline as free as possible from unsaturated hydrocarbons appears to be desired, although it is realized that unsaturated hydrocarbons in gasoline possess certain qualities which render their presence advantageous. It is therefore suggested that a possible method for eking out a diminishing supply of gasoline might be to obtain the latter by the destructive distillation of asphalt and blend the unsaturated naphtha so obtained with more saturated naphtha obtained from petroleum.

W. J. A. Butterfield [1] discusses the possible sources of supply of motor fuel within the British Empire, including asphalt. Very little crude petroleum, it is stated, is available, and the chief sources are oil shale and bituminous coal or cannel. Motor spirit could be obtained according to Butterfield, by cracking the native (asphalt) residues in Canada, the East Indies, and Egypt.

Everett Smith [2] distills asphalt by placing the material in a very thin layer (4–6″ thick) in a long, wide and shallow retort and subjecting the latter to a temperature of about 800° F. (427° C.) until no more distillate is obtained.

Kharickov [3] considers the natural asphalts as primary products, and that the crude petroleums in nature are not produced by high heat and rapid decomposition, but by very slow and spontaneous decomposition of the asphalts. The decomposition products of natural asphalts as decomposed in the laboratory showed, it is stated, in quality and quantity of fractions, much resemblance to petroleum products. The fractions from 150° to 270° C. (302°–518° F.) after refining with sulphuric acid and caustic soda were stated to be very similar to light oil. The residue was like masut (still residue obtained in distilling Russian petroleum).

[1] J. S. C. I. 1913, 819, 416; Times Eng. Suppl. July 23, 1913.

[2] Chem. Abs. 1909, 2380; British Patent 27,335, Dec. 11, 1907.

[3] Chem. Abs. 1910, 248; Gorny J. May (1909); through Chem. Rev. Fett — Harz-Ind. 11, 279.

Kharichov [1] observes that a Syrian asphalt containing no sulphur and 1.2 per cent nitrogen of density 1.104 at 15° C. (59° F.) on dry distillation [between 300° and 360° C.] (572° and 680° F.) gave 4.8 per cent water (containing ammonia) 45.9 per cent liquid distillate of density 0.8683 at 15° C. (59° F.), 43.5 per cent of coke and 6.3 per cent gas and loss. The liquid distillate was dark, resembling crude petroleum. On fractional distillation it gave.

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  0 – 80° C. (  0–176° F.)  2.0  per cent
 87°–190° C. (189–212° F.)  5 16 per cent
100°–150° C. (212–302° F.)  6.42 per cent
150°–220° C. (302–428° F )  20.56 per cent
220°–270° C. (428–518° F.) 17.48 per cent
Residue...................48.08 per cent
Loss..  ...................  0.03
                           ——
                          99.63
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F. B. Deakin [2] distills crude petroleum, gas oil, residuals of petroleum or asphalt, for the production of lighter hydrocarbons and cools the upper part of the retort by the controlled application of water in order to condense the high-boiling constituents of the vapors while allowing the lighter fractions to escape to the condenser. The retort is cooled by applying a spray of liquid to the outside, or by internal means such as cooling tubes. A cooling tank surrounds the vapor outlet pipe which is inclined upwards. The coke which is formed is maintained in suspension by a scraper. The heavier constituents of the liquid are removed by a pipe communicating with a chamber in the retort which is closed at the top and open at the bottom; the retort is heated by the combustion of the oils so withdrawn. To prevent the transmission of heat to the upper portion of the retort, the lower and upper walls are separated by sheets of asbestos.

A. Rollason [3] holds the view that in the carbonization or distillation of coals, cannels and shales whose organic constituents contain a relatively large proportion of oxygen, this oxygen exerts an oxidizing action during the distillation, combines for the most part with hydrogen and passes off in the form of water. In other words, the presence of a high percentage of oxygen in the bituminous matter is said to diminish greatly the yield of hydrocarbon distillates, for example, oils of the benzol series, in that the oxygen unites (to form water) with much of the hydrogen that would otherwise appear as light hydrocarbon

[1] Chem. Abs. 1910, 1235; Revue pétrole; through Oesterr. Chem. Ltg. 27,190.

[2] Chem. Abs. 1917, 3427; British Patent 108,946, Aug. 16, 1916.

[3] British Patent 19,697, Sept. 1, 1913.

distillates. It is sought to overcome this disadvantage by grinding the coal or shale and mixing it, previous to distillation, with a proportion of limestone proportionate to the oxygen content of the bitumen, for example, 3 to 5 per cent of limestone to coal containing 8 to $13\frac{1}{2}$ per cent of oxygen. The carbon dioxide evolved by the limestone during heating is claimed to prevent very largely (by dilution) the union of oxygen and hydrogen to form water.

The large deposits of gilsonite in Utah appear to offer a source of naphtha, particularly varnish makers' and painters' naphtha and turpentine substitutes. It may be said that the naphtha obtained is the product of a cracking operation since it is not contained as such in the original material. Nevertheless, when refined, it is free from objectionable odor and especially suited for solvent purposes. It is believed to contain a considerable proportion of hydroaromatic hydrocarbons.

On the basis of the experience of one of the authors it may be said that about 10 per cent of naphtha, based on the raw material (boiling $0°$ to $400°$ F. ($204°$ C.)) may be obtained by destructively distilling the original gilsonite and fractionating this distillate, and it is believed that this amount can be increased by cracking heavier distillates. This naphtha is believed to contain representatives of the C_nH_{2n} and C_nH_{2n-2} series of hydrocarbons. It resembles in the constitutions of a part of its constituents the terpene or C_nH_{2n-4} series. Although it is largely unsaturated, it possesses, after simple refining, a very good odor. In several respects the properties are analogous to those of terpene hydrocarbons. A portion of this naphtha can be easily condensed by means of nitric acid and other condensing agents,[1] according to **Forrest** and **Meigs,** into resinous bodies which blend well with pyroxylin. In this respect, also, the portion of the naphtha which condenses resembles turpentine. Indeed, during treatment with nitric acid, an odor of pinene is evolved. The distillation of the gilsonite itself offers no more difficulties than the distillation of crude oil and can readily be accomplished in an ordinary coking still. From 25 to 30 per cent of coke and in the neighborhood of 10 per cent of gas is obtained, the rest being liquid distillate. The original material is practically pure bitumen. It breaks down very readily on the application of heat, at atmospheric pressure. Moreover, the intermediate burning oil fractions are also very susceptible to cracking to yield naphtha. The fact that the original gilsonite is so nearly pure hydrocarbon renders it commercially feasible to transport the material a considerable distance from its source to refineries. Sufficient gas, largely methane, is produced

[1] Chem. Abs. 1919, 2140; U. S. Patent 1,305,790, June 3, 1919.

during the distillation, to provide the necessary fuel. A considerable amount of ammonia is also obtained.

C. F. Mabery [1] states that samples of bituminous (Deerfield) coal, gilsonite, and grahamite have the following proximate composition:

	Gilsonite	Grahamite	Coal
	%	%	%
Volatile matter	56 0	44 52	38 13
Fixed carbon	44 0	38 99	58.29
Ash	....	5.51	2 31
Sulphur	0 02	2 07	0 69
Nitrogen	1.05	.....	0 05

The bituminous coal, when distilled in vacuo in an electrically heated iron still, yielded 5.6 per cent of distillate, consisting largely of a number of hydrocarbons which closely resembled those forming the larger part of the adjacent Mahone petroleum. No hydrocarbons of the series C_nH_{2n-2} were found in the coal distillates, but were present in the petroleum, while hydrocarbons of the series C_nH_{2n}, which are generally present in petroleum, although not in Mahone petroleum, were constituents of the coal distillates. The sample of gilsonite (from Utah) yielded from 50 to 56 per cent of distillate containing hydrocarbons of the series C_nH_{2n} and C_nH_{2n-2}, which resembled the same hydrocarbons in petroleum, and also a series of unsaturated hydrocarbons, which readily absorbed oxygen and became of a dark color. The deep color of crude petroleums is said probably to be due to absorption of oxygen by similar unsaturated hydrocarbons such as nonylene found by **Mabery** and **Quayle** in Canadian petroleum. Most varieties of petroleum contain small proportions of these hydrocarbons, which have a peculiar odor, and can be readily extracted with sulphuric acid. The sample of grahamite resembled the bituminous coal in appearance. When distilled under reduced pressure of 20 mm. it yielded 13.5 per cent of distillate with specific gravity 0.85 at 20° C. (68° F.), which had an odor resembling that of petroleum distillates. It contained a series of hydrocarbons closely resembling those obtained from gilsonite, suggesting a common origin. The large proportion of nitrogen compounds present in gilsonite, however, indicates that it stands in closer relationship to petroleum than does grahamite, which only contains a trace of nitrogen bases.

[1] J. S. C. I. 1917, 1123; J. Amer. Chem. Soc. 1917, 39, 2015–2037.

Mabery [1] believes that it is improbable that the distillate obtained from gilsonite at atmospheric pressure contains members of the series C_nH_{2n+2} lower than the solid paraffins. In the distillates refined with sulphuric acid and soda, Mabery [2] has found hydrocarbons of the formulæ C_nH_{2n} and C_nH_{2n-2} respectively, which latter may be cyclic unsaturated hydrocarbons. In the oils soluble in sulphuric acid hydrocarbons of the C_nH_{2n} series were found (undoubtedly olefins). Mabery has therefore found hydrocarbons of the C_nH_{2n} series in both the acid refined oils and also in those oils soluble in sulphuric acid. ·

Mabery [3] obtained on the laboratory scale a maximum yield of 56 per cent under reduced pressure of distillate from gilsonite.

Bardwell, Berryman, Brighton, and Kuhre [4] state that in 1910 the production of gilsonite was 30,000 tons; in 1912, over 50,000 tons, worth about $20.00 a ton (f.o.b. Utah). These writers have studied the occurrence, properties and uses of the asphalts of Utah and state that gilsonite, tabbyite, wurtzilite, ozokerite and rock asphalt are all found in quantity.

Bardwell and his co-workers have distilled the above asphalts at atmospheric pressure and have compared the results obtained with those obtained in a similar manner with Trinidad and Bermudez asphalts. The results are shown in Table 6.

TABLE 6

Substance	Trin.	Ber.	Gal.	Tab	Wur.	Ozok.
0-150° C. (0-302° F.) ..	14 93	9 89	9 34	3 12	16 15	0 21
150-200° C. (302-392° F.) .	10.42	7.99	5 34	11 93	21.70	8.91
200-250° C. (392-482° F.) ..	2 26	16 08	12 84	24 87	22 82	8.38
250-300° C. (482-572° F.) ..	.....	21 12	28 99	13 21	0 91	17 69
300-350° C. (572-662° F.) .	....	......	.....	4 77	.....	25.89
350-400° C. (662-752° F.) .	.....	.....	..	.....	.....	26 85
Total Volatile	27.61	55.08	56 51[5]	57.90	61.58	87.93
Fixed Carbon	36 69	39 60	43 13	37.45	36 92	10 03
Ash	35.70	5.32	0 36[6]	4 65	1 50	0 04

Aylsworth and Dyer [7] describe a retort which distills viscous bodies including heavy oil residues, pitch and asphalt, continuously, under atmospheric pressure, vacuum or super-atmospheric pressure. It con-

[1] J. Am. Chem. Soc. 1917, 2020. [2] *Loc cit* p 2022.
[3] *Loc. cit.* p. 2021. [4] J. Ind. Eng. Chem. 1913, 973-976.
[5] Higher yields are commercially obtainable (Meigs).
[6] Attention is called to the very low per cent of ash.
[7] U. S. Patent 1,079,093, Nov. 18, 1913.

sists, essentially, of a vertical chamber through which the material to be distilled, mixed with pieces of solid refractory substances, passes in a downward direction, by gravity feed. Products of distillation are removed by a pump and the uncondensed gases are reheated and returned to the reaction zone, if the distillation is carried out at atmospheric pressure.

W. A. Hall[1] distills heavy oils, oil residues and solid bitumens as follows: the oil is mixed with not less than its own weight of coke or similar porous material and heated by external heat to about 475° C. (887° F.) and the vapors are condensed. The coke may be heated in a retort into which the oil is constantly introduced in regulated proportion. Under these conditions the distillates of low boiling point closely correspond in composition, whatever the nature of the original crude oil.

Hall states that when this process is carried out starting with a thick viscous bituminous oil, such as the crude oils of Mexico or their heavy distillates or residues, which may be still bottoms or even solid asphaltum (bitumen) with gravities approximating to or in excess of that of water, a thin limpid oil is obtained of from 0.845 to 0.895 gravity which does not thicken or congeal even at 0° C. In practicing the process, the heavy bituminous oil is first heated to render it thin and is then mixed with sufficient coke to produce a semi-dry mass and this mass is retorted, giving a yield of oil from 75 to 85 per cent in volume of the total amount treated, the balance (15 to 25 per cent) being dry coke and left in the retort. This method can, it is said, be economically practiced where fuel is inexpensive, but as from two to three parts of coke are required to one part of oil, all this extraneous material must be heated. Moreover the process is intermittent and requires the cleaning of the still or retort when the operation is completed.

Another objection to that particular method is the great difficulty of imparting heat from external sources through the heavy mass of oil-saturated coke, which acts as a non-conductor or insulator of heat. Thus comparatively small diameter retorts are required.

These disadvantages are said to be overcome [2] by placing the mixture of heavy bitumen and coke in the upper end of a tall gas producer. Here distillation takes place by the action of the non-oxidizing hot combustion products formed by the burning of the coke in the lower part of the producer. It is stated that with very bituminous oils, the

[1] J. S. C. I. 1916, 919; British Patents 4598, Mar. 24, 1915; 7209, May 13, 1915; and 7778, May 25, 1915.

[2] J. S. C. I. 1916, 919; Chem. Abs. 1916, 3156; U. S. Patent 1,247,671, Nov. 27, 1917; British Patent 8836, June 15, 1915.

coke which the oil itself furnishes is sufficient for the fuel requirements
of the process.

G. H. Ashley [1] describes the Santo Tomas Cannel Coal of Webb
County, Texas, and indicates its possibilities as a source of motor fuel.

It is stated that this coal [2] is of unique interest, both economically and geo-
logically. It is of economic interest because it is probably the largest body of
cannel coal of bituminous rank in the United States, if not in the world. It is
of geologic interest because it is not the high-moisture, soft brown lignite which is
characteristic of coal beds of the same age in the central and eastern parts of the
state, but a low-moisture coal almost as hard as anthracite, resisting weathering
like an ordinary bituminous coal and sold on Government contracts under a guar-
anty of 12,500 British thermal units on "dry coal." As a cannel coal it has special
interest because on distillation such coal yields a much larger proportion of oil
at a low temperature or of gas at a high temperature than ordinary bituminous
coal, and at present and probably for some time in the future these products may
be in great demand in the growing chemical industry of the United States. Tests
have shown that although cannel coal yields a large percentage of oil when dis-
tilled at a low temperature, yet this oil contains so large a percentage of un-
saturated hydrocarbons, as to be unavailable as a source of benzol and toluol
products. Most deposits of cannel coal are too small to justify the erection
near by of a distillation plant of any considerable size for their utilization, but
the amount of coal already in sight in this district warrants its investigation
by those interested in chemical industries. A by-product of mining here is the
large amount of clay that has to be removed in the mining operations. The clay
already removed forms very large dumps and lies ready for use in the manufacture
of any clay products for which it may be suited. It will probably not be found
suitable for high-grade fire brick, but rather for vitrified ware, sewer pipe, drain-
tile, and possibly paving brick.

An interesting feature of this coal [3] is said to be the large percentage of nitro-
gen shown in certain of the analyses. If those analyses are correct this coal con-
tains more nitrogen than any other coal in the United States. The samples taken
by Ashley have not yielded so high a percentage of nitrogen as some of the older
samples. Most coals contain between 0.5 and 1.5 per cent of nitrogen, but in some
areas, notably parts of Washington and northern Tennessee, many of the coals
contain 2 per cent and some run as high as 3.5 per cent of nitrogen in the sample
as received. At first sight these figures would seem to indicate, it is stated, that
the Santo Tomas coal might be of great value in the production of ammonia but,
the oil and gas obtained from cannel coal are given off so readily and at so low a
temperature that they consist largely of unsaturated hydrocarbons without combined
nitrogen.

The tests of the Santo Tomas coal by low temperature distillation
by the Bureau of Mines gave the following results: [4]

[1] U. S. Geological Survey, Bulletin 691 — I, July 25, 1918 (Contributions to
economic geology, 1918, Part II, pp. 251-270).

[2] *Ibid.* p. 251.   [3] *Ibid.* p. 256.   [4] *Ibid.* p. 260.

Oil:

  Gallons per ton 52.2
  Per cent by weight of coal 20.2

  Specific gravity at $\dfrac{60°}{60}$ F 0.938

Gas:
  Non-liquid at 60° F.
  Cubic feet per ton, collected over water, at 0° C. and 706 milli-
    meters pressure 5672

Water:
  Per cent by weight of coal condensed 9.5

Loss in distillation:
  Per cent by weight 44.3

Ammonia:
  Not determined.

This yield of 52.5 gallons a ton may be compared [1] with 59.4 and 37.3 gallons a ton obtained by two tests under the same conditions of coal from Cannelton, Pa., which in the past has been successfully used in the production of oil. This field, on account of its large size and the abundance of coal in sight, would seem to be a favorable place in which to determine by experiments what can be done with such an oil by distillation at different temperatures and at different pressures, and how the oils and tars obtained may be made available for gasoline and other much needed products.

J. C. Ingram [2] distilled four cannel coals (from Missouri and Illinois) and two bituminous coals, under similar conditions, in a horizontal gas-fired retort, the charge in each case weighing from 25 to 35 pounds. The gas produced was measured and collected after passing successively through two condensers, and three gas-washers containing water. The oils obtained from the cannel coals were fractionated to yield gasoline (up to 150° C., 302° F.), kerosene (150–300° C., 302–572° F.); and lubricating oil (above 300° C., 572° F.), and coke. The bituminous coals yielded small quantities of tar (5.35 to 12.5 gal. per ton) composed of paraffins, olefins, aromatic substances, and a large proportion of bitumens. The cannel coals gave comparatively large amounts chiefly of liquid and solid hydrocarbons of the methane and olefin series, together with cresols and asphaltic bodies. The cannel oils averaged about 11 per cent gasoline (supposed to be similar to that produced by the cracking process), 40 per cent kerosene and 40

[1] *Ibid.* p. 261.
[2] J. S. C. I. 1917, 1172; School of Mines and Met. Univ. of Missouri, Bull. No. 4, vol. 3, May, 1917.

per cent lubricating oil containing 25 per cent of solid paraffins. Maximum gasoline production was obtained by distilling between 450° and 550° C. (842°–1022° F.). Hard paraffin and kerosene were formed in largest quantity between 550° and 650° C. (1022° 1202° F.), while above 650° C. soft paraffins, heavy oils, kerosene, and bitumens were the main products. A yield of 3500 and 8100 cubic feet per ton of very rich gas was obtained from the cannel coals, the time of maximum production being between the fifth and sixth half hours. Only one sample gave a saleable coke.

APPENDIX

STATISTICS ON PETROLEUM PRODUCTS [1]

Accompanying the regular monthly report on petroleum refinery products, the United States Bureau of Mines issues the following review of the gasoline situation for the first four months of 1920, with comparisons of the same periods of the three previous years:

During the months, January, February, March, and April, 1920, the production of gasoline increased 1,352,890 gallons daily or $13\frac{1}{2}$ per cent; whereas, the domestic consumption of gasoline increased 2,148,920 gallons daily, or 33 per cent, indicating a far greater increase in consumption than in production. Consumption increased 796,030 gallons per day more than production.

Stocks of gasoline at the end of April, 1920, were 49,936,474 gallons more than for the corresponding period of 1919, or, approximately, $8\frac{1}{2}$ per cent greater. Stocks for the end of April, 1918, represented sixty days' production; in 1919 the stocks represented fifty-nine days' production; whereas, in 1920 the stocks represented fifty-six days' production.

Exports during the first four months of 1920 increased by 246,802 gallons daily, which, however, is still less by 142,852 gallons daily than for the same period in 1918.

The imports of gasoline for the first four months of 1920 — the largest on record — were approximately 100 per cent increase over 1918 during the same period, but still constituted less than 1 per cent of the total gasoline production.

Shipments to our insular possessions — Alaska, Hawaii, Porto Rico, and the Philippines during the first four months of 1920 were approximately 37,000 gallons per day. During the same period for 1919 they were 43,000 gallons per day.

The following tabulation summarizes the gasoline situation for the last four years:

SUMMARY. — GASOLINE STATISTICS

First Four Months of Years 1917, 1918, 1919, and 1920
Daily Average

Year	Production (Gallons)	Domestic Consumption (Gallons)	Stocks at end of April (Gallons)	Equivalent days' production
1917	6,923,058	. . . . . .	. . . .	. .
1918	8,594,882	6,411,452	509,197,134	60
1919	10,068,953	6,442,992	593,616,170	59
1920	11,421,843	8,591,912	643,552,644	56

Imports and Exports
Daily Average

Year	Imports (Gallons)	Exports (Gallons)	Shipments to insular possessions (Gallons)
1917	22,745	993,034	37,579
1918	63,356	1,407,667	37,960
1919	49,991	1,018,013	43,98
1920	98,653	1,264,815	37,659

DEPARTMENT OF THE INTERIOR   BUREAU OF MINES

Stocks on Hand at the Refineries

1917	October 31	November 30	December 31
Crude oil (bbl.)..	12,123,687	11,818,160	11,638,433
Oils purchased to be re-run (bbl.).	793,402	786,554	973,322
Gasoline (gal.)	320,203,770	360,241,135	412,256,833
Kerosene (gal.).	555,867,262	537,168,089	497,750,082
Gas and fuel (gal.).	690,209,380	630,190,045	577,899,112
Lubricating oil (gal.)	125,081,023	130,834,040	136,855,342
Wax (lbs.)	112,802,614	122,766,409	135,059,927
Coke (tons)	8,823	9,667	7,585
Asphaltum (tons)	61,994	53,650	52,860
Miscellaneous (gal.).	258,439,112	248,731,757	261,363,964

.TAIL OF MISCELLANEOUS OILS PRODUCED DURING 1919

Reported on Monthly Refinery Report under "Miscellaneous"

	Gallons
Binder.	1,683,451
Flux .	31,284,816
Ink oil....	105
Medicinal oils	1,129,932
Petrolatum	6,421,178
Road	77,637,992
Roofers' wax	158,250
Sludge products .	14,994,298
Paint	478
Paint Products.	75,637
Acid Oil	3,765,703
Distillate	571,238,381
Motor fuel	57,893
Motor spirit ..	58,328,036
Pitch.	473,746
Residue	39,546
Slops	379,052
Tailings	19,325,735
Tar.	3,545,407
Tops.	108,955,510
Unfinished	376,229,215
Wash out	122,380
Wax tailings	3,017,039
Total..................................	1,278,863,780

DEPARTMENT OF THE INTERIOR.   BUREAU OF MINES

Detail of Oil Run to Refinery Stills in 1919

1919	Crude oil (bbl.)	Other oils				Total oils run (bbl.)
		Purchased and re-run (bbl.)	Own oils re-run (bbl.)	Casing-head Gasoline (bbl.)	Total other oils (bbl.)	
January	26,967,332	2,396,789	1,273,661	249,042	3,919,492	30,886,824
February	25,232,876	2,160,992	1,592,416	243,617	3,997,025	29,229,901
March...	27,866,775	1,991,025	1,081,589	279,207	3,351,821	31,218,596
April ...	27,775,217	2,544,935	1,339,954	312,561	4,197,450	31,972,667
May ..	30,267,227	2,458,203	2,007,840	254,877	4,720,920	34,988,147
June	28,920,764	1,660,390	2,136,301	195,318	3,992,009	32,912,773
July......	31,202,522	2,202,216	1,409,565	151,176	3,762,957	34,965,479
August	32,362,057	2,203,603	1,316,653	193,300	3,713,556	36,075,613
September	32,601,044	1,635,342	1,348,082	233,465	3,216,889	35,817,933
October .	33,682,968	1,932,524	1,316,951	241,619	3,491,094	37,174,062
November.	32,213,754	1,857,372	1,454,960	266,982	3,579,314	35,793,068
December.	32,427,617	2,500,159	984,313	335,617	3,820,089	36,247,706
Total.	361,520,153	25,543,550	17,262,285	2,956,781	45,762,616	407,282,769·

Refined Oils Situation for 1919 Summarized

Accompanying are statistics of the petroleum refining industry in the United States, collected and compiled by the Bureau of Mines for the year 1919.

At the end of December there were 292 refineries operating, with a daily capacity of 1,356,355 barrels of crude oil.   Comparison with the years 1917 and 1918 follows:

	Operating·	Daily Capacity
1917.........	215	1,157,875 bbl.
1918........................ .	267	1,226,175 "
1919.........	292	1,356,355 "

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES

Stocks on Hand at Refineries December 31, 1918

1918	East Coast (N.Y., Phila and Baltimore)	Pa., N.Y., East Ohio and West Va	W Ohio, Ind., Ill., Ky and Tenn	Oklahoma and Kansas	Texas and Louisiana	Colorado and Wyoming	California	Total
Crude oil (bbl)	2,591,190	1,111,631	633,695	2,230,092	6,737,350	752,750	1,693,060	15,749,771
Oils purchased to be re-run (bbl)	264,222	79,449	566,547	15,337	59,987	80,032	234,244	1,300,018
Gasoline (gal)	60,648,988	19,385,809	60,362,188	44,313,435	58,723,065	21,827,173	32,065,025	297,326,983
Kerosene (gal)	78,062,139	14,857,026	24,353,873	19,398,987	219,488,605	12,198,283	11,528,912	380,117,829
Gas and fuel (gal)	133,338,573	27,060,623	32,231,010	109,828,305	152,707,300	30,888,967	172,946,579	659,001,357
Lubricating (gal)	59,827,149	23,561,384	13,783,139	9,480,877	23,656,327	491,895	8,052,803	138,853,574
Wax (lb)	93,866,023	24,424,293	19,117,331	5,249,375	36,232,544	505,916	172,060	199,657,542
Coke (ton)	5,910	577	2,669	4,402	5,048	3,999	......	22,605
Asphalt (ton)	23,038	2,620	5,985	18	37,229	17	7,951	76,858
Miscellaneous (gal)	126,353,098	19,119,426	46,778,887	43,961,174	132,374,373	9,388,717	99,808,065	477,783,740

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES

Stocks on Hand at Refineries December 31, 1919

1919	East Coast, (N. Y., Phila. and N. Y., and Baltimore)	Pa., N. Y., East Ohio, and W. Va.	W. Ohio, Ind., Ill., Ky. and Tenn.	Oklahoma and Kansas	Texas and Louisiana	Colorado and Wyoming	California	Total stocks end of		
								December, 1919	December, 1918	December, 1917
Crude oil (bbl)	1,979,072	689,051	979,388	1,860,314	5,627,242	649,289	1,349,729	13,143,285	15,749,771	11,638,433
Oils purchased to be re-run (bbl)	371,378	72,347	133,087	15,926	143,966	24,573	380,107	1,141,384	?,300,018	973,322
Gasoline (gal.)	94,510,003	22,754,624	76,350,941	83,871,386	135,765,729	17,993,383	15,538,365	446,793,431	297,326,983	412,256,833
Kerosene (gal.)	102,880,801	16,387,900	40,693,539	22,079,364	133,269,896	11,086,754	12,921,433	339,319,690	380,117,829	497,750,082
Gas and fuel (gal.)	71,291,924	22,437,724	24,722,461	153,707,545	206,452,059	19,151,243	216,358,499	714,124,455	659,001,357	577,899,112
Lubricating (gal.)	52,342,559	27,102,441	14,516,417	13,370,290	18,356,996	275,622	11,354,609	137,318,934	138,853,574	136,855,342
Wax (lb.)	63,340,005	27,916,508	35,004,911	99,014,031	76,869,924	10?,168	180,957	212,461,594	199,657,542	135,059,927
Coke (ton)	9,160	941	5,828	1,948	2,905	364	....	21,146	22,605	7,585
Asphalt (ton)	25,255	1,118	4,133	17	33,686		9,246	73,449	76,858	77,452
Miscellaneous (gal.)	62,070,809	25,189,628	45,461,792	48,930,336	174,833,446	18,615,607	26,781,856	401,883,474	477,783,740	261,363,964

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES

Stocks on Hand at Refineries January 31, 1920

1920	East Coast (N.Y., Phila and Baltimore)	Pa., N.Y., East Ohio, and W. Va.	W. Ohio, Ind., Ill., Ky. and Tenn	Oklahoma and Kansas	Texas and Louisiana	Colorado and Wyoming	California	Total stocks end of		
								January, 1920	January, 1919	January, 1918
Crude oil (bbl.)	1,717,479	631,890	992,549	2,115,375	5,792,861	617,454	1,333,119	13,200,727	15,380,185	12,436,923
Oils purchased to be re-run (bbl.)	284,374	59,056	147,312	3,089	41,135	13,883	417,704	966,503	1,088,264	799,512
Gasoline (gal.)	103,536,553	26,750,717	96,947,278	102,915,997	142,830,836	27,324,418	15,628,565	515,934,364	383,212,692	473,165,166
Kerosene (gal.)	79,191,752	13,618,854	49,158,867	25,348,823	129,995,259	12,406,372	17,828,719	327,548,646	332,393,181	438,172,395
Gas and fuel (gal.)	58,594,112	20,521,069	24,782,658	128,871,250	184,163,070	17,394,670	217,754,072	652,080,901	646,111,414	550,003,875
Lubricating (gal.)	51,450,356	26,463,677	14,367,031	14,633,911	19,584,528	626,128	14,554,346	141,690,177	154,370,431	143,679,068
Wax (lb.)	56,423,019	26,466,506	31,962,426	4,522,726	83,106,524	707,865	472,966	203,662,032	189,064,329	154,749,374
Coke (ton)	10,226	914	7,006	2,432	572	86		21,236	28,732	8,010
Asphalt (ton)	24,035	1,033	4,016	16	33,110		9,826	72,036	93,027	92,209
Miscellaneous (gal.)	56,437,854	21,409,715	46,147,233	50,632,173	175,026,843	12,448,230	28,931,289	391,033,357	483,944,833	230,941,788

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES.

Stocks on Hand at Refineries February 29, 1920

1920	East Coast (N. Y., Phila and Baltimore)	Pa., N. Y., East Ohio, and W. Va.	W. Ohio, Ind., Ill., Ky. and Tenn	Oklahoma and Kansas	Texas and Louisiana	Colorado and Wyoming	California	Total stocks end of		
								February, 1920	February, 1919	February, 1918
Crude oil (bbl.)	1,878,806	733,420	966,583	2,073,536	5,966,367	338,417	1,323,470	13,500,599	14,820,601	11,692,890
Oils purchased to be re-run (bbl.)	206,306	49,841	82,021	19,306	....	23,953	421,593	863,220	1,176,483	849,935
Gasoline (gal.)	118,821,037	32,997,612	118,889,818	98,237,553	140,478,023	45,386,472	18,185,074	562,996,489	458,449,187	523,727,009
Kerosene (gal.)	80,279,236	12,921,586	34,399,298	26,149,961	130,941,052	13,476,450	11,953,359	330,120,942	303,062,436	413,508,407
Gas and fuel (gal.)	32,739,887	16,731,491	25,067,249	102,427,266	136,302,538	17,973,985	219,057,709	590,322,125	692,816,000	506,662,587
Lubricating (gal.)	47,505,679	26,047,753	15,104,469	11,431,269	20,200,908	508,228	11,960,938	132,759,244	152,297,163	151,938,153
Wax (lb.)	48,072,300	24,703,518	35,869,536	4,213,413	83,782,497	912,737	433,500	197,996,501	209,908,707	149,719,765
Coke (ton)	9,706	1,050	9,121	546	461	825	....	21,709	33,716	9,885
Asphalt (ton)	26,284	773	2,841	16	28,104	......	12,047	70,067	102,547	98,695
Miscellaneous (gal.)	64,286,166	16,724,363	54,583,073	57,472,994	170,228,673	12,727,541	29,365,659	405,588,469	500,413,825	230,023,915

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES.

Stocks on Hand at Refineries, March 31, 1920

1920	East Coast (N.Y., Phila. and Baltimore)	Pa., N.Y., East Ohio, and W.Va	W.Ohio, Ind., Ill., Ky. and Tenn	Oklahoma and Kansas	Texas and Louisiana	Colorado and Wyoming	California	Total stocks end of		
								March, 1920	March, 1919	March, 1918
Crude oil (bbl)	2,002,987	980,859	1,026,200	2,307,411	6,055,420	527,377	1,446,196	14,346,458	15,106,361	13,122,241
Oils purchased to be re-run (bbl)	219,060	37,511	84,577	3,364	10,000	18,636	433,025	806,479	1,121,963	922,360
Gasoline (gal)	139,149,472	38,569,900	135,469,380	101,185,377	151,988,968	40,401,197	19,628,752	626,393,046	546,062,429	526,382,386
Kerosene (gal)	86,669,474	14,070,563	33,695,656	31,134,009	124,327,217	14,971,423	9,748,775	334,617,117	294,677,623	356,580,540
Gas and fuel (gal)	56,505,645	13,708,992	20,986,502	90,753,126	160,339,410	16,686,057	221,093,126	580,182,858	749,067,806	483,447,727
Lubricating (gal)	48,318,714	24,960,992	13,534,045	9,136,554	19,810,415	643,312	14,226,565	130,630,597	165,495,254	146,572,308
Wax (lb)	45,700,670	21,026,054	39,033,277	4,352,879	56,556,673	823,783	534,682	168,030,018	235,588,922	162,221,741
Coke (ton)	4919	544	8,787	1,090	413	1,489		17,542	37,642	11,301
Asphalt (ton)	21,871	848	5,754	16	44,911		14,320	87,720	113,949	107,122
Miscellaneous (gal)	70,228,450	17,871,020	60,242,000	65,033,716	159,134,526	15,129,242	41,110,706	428,749,660	468,035,524	238,659,787

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES.

Stocks on Hand at Refineries End of April, 1920

1920	East Coast (N.Y., Phila. and Baltimore)	Pa., N.Y., East Ohio, and W. Va	W. Ohio, Ind., Ill., Ky. and Tenn	Oklahoma and Kansas	Texas and Louisiana	Colorado and Wyoming	California	Total stocks end of		
								April, 1920	April, 1919	April, 1918
Crude oil (bbl)	2,468,418	960,962	1,111,719	2,331,576	6,396,616	480,749	1,386,651	15,145,691	15,184,844	12,600,062
Oils purchased to be re-run (bbl)	288,543	33,476	93,063			22,742	321,114	758,938	980,597	954,205
Gasoline (gal)	132,417,296	40,212,961	142,732,449	95,774,688	165,358,571	42,476,289	24,580,300	643,552,644	593,616,170	509,197,134
Kerosene (gal)	100,218,544	16,948,995	51,224,148	32,306,497	151,762,506	15,385,814	8,511,616	376,358,123	276,356,837	393,527,476
Gas and fuel (gal)	62,014,790	16,222,761	24,979,947	100,696,703	133,672,680	17,931,499	235,168,629	590,687,009	807,895,498	471,644,479
Lubricating (gal)	50,895,257	28,342,689	14,640,036	11,590,409	20,102,045	598,398	14,187,138	140,355,972	170,122,088	144,383,212
Wax (lb)	47,702,914	23,361,032	42,408,028	4,476,225	68,455,862	1,772,497	644,354	188,170,912	249,351,315	151,228,317
Coke (ton)	5,442	1,433	9,724	1,475	559	1,061		19,694	45,601	13,109
Asphalt (ton)	28,431	886	4,798	9	27,457		16,692	78,273	118,863	101,328
Miscellaneous (gal.) ...	80,782,702	18,196,060	59,493,255	79,895,011	186,672,736	16,011,617	46,880,776	487,932,157	480,607,249	248,260,551

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES

Output of Refineries in the United States by Months

1917	January	February	March	April	May	June	July	August	September	Total
Crude run (bbl)	23,157,349	21,570,486	24,460,800	21,410,623	25,707,420	24,788,484	26,064,350	27,209,383	26,867,024	224,205,919
Oils purchased and re-run (bbl)							2,435,533	2,376,580	2,632,988	7,445,101
Gasoline (gal)	180,169,526	172,704,579	203,677,089	213,131,064	225,655,440	219,843,859	238,309,073	249,365,362	250,348,628	1,962,205,420
Kerosene (gal)	120,735,586	113,369,304	141,123,626	140,594,030	132,850,318	135,738,427	157,259,832	145,678,500	138,769,343	1,226,118,966
Gas and fuel (gal)	443,955,903	424,115,567	467,378,504	439,724,364	481,281,431	468,190,931	585,932,568	620,029,060	618,067,279	4,548,676,207
Lubricating (gal)	57,954,874	51,831,577	60,848,934	59,546,525	62,247,738	57,928,393	62,307,742	62,347,947	58,686,398	533,700,128
Wax (lb)	34,084,178	31,439,730	35,105,016	35,267,563	34,318,668	33,760,558	36,548,059	38,832,839	37,440,127	316,796,738
Coke (ton)	37,622	35,672	41,968	40,084	37,919	36,458	39,814	43,787	40,101	333,425
Asphalt (ton)	48,860	39,795	51,265	50,404	63,692	66,780	65,272	73,878	62,520	522,475
Miscellaneous (gal.)	21,089,919	20,013,294	21,217,958	24,647,645	25,874,828	26,623,539	90,637,733	91,115,337	79,127,811	400,348,067
Loss (bbl.)	844,007	864,931	794,009	887,243	886,767	934,882	1,060,020	1,241,281	1,130,900	8,644,040

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES

Output of Refineries in the United States by Months

1917	First nine months	October	November	December	Total, 1917	Daily Average
Crude run (bbl)	224,295,919	26,971,980	25,516,693	24,534,726	301,319,318	828,532
Oils purchased and re-run (bbl)......	7,445,101	2,863,518	2,519,700	2,069,351	14,897,670	¹40,816
Gasoline (gal)	1,962,205,420	265,634,890	258,696,514	243,175,209	2,729,712,033	7,478,663
Kerosene (gal)	1,226,118,966	135,775,025	121,133,610	118,987,502	1,602,015,103	4,389,082
Gas and fuel (gal)	4,548,676,207	608,327,006	580,140,259	531,287,109	6,288,430,581	17,228,577
Lubricating (gal.)......	533,700,128	66,289,783	62,631,249	59,023,661	721,644,821	1,977,109
Wax (lb.)......	315,796,738	46,623,624	39,502,105	38,185,497	441,107,964	1,208,515
Coke (ton)......	353,425	45,746	42,708	42,301	484,180	1,327
Asphalt (ton)......	522,475	61,579	58,849	47,376	690,279	1,891
Miscellaneous (gal)......	400,348,067	90,341,931	85,863,880	86,595,992	663,149,870	1,816,849
Loss (bbl)......	8,644,040	1,299,477	1,147,662	1,182,671	12,273,850	33,627

¹ No account of this item for first six months.

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES

Output of Refineries in the United States for the Year 1918

1918	Crude run (bbl.)	Oils Purchased and re-run (bbl.)	Gasoline (gal.)	Kerosene (gal.)	Gas and fuel (gal.)	Lubricating (gal.)	Wax (lb.)	Coke (ton)	Asphalt (ton)	Miscellaneous (gal.)	Losses (bbl.)
East Coast	64,119,528	7,330,083	718,720,111	485,559,229	1,118,998,731	257,112,655	215,791,443	222,644	270,172	78,617,550	3,631,988
Penna.	18,894,510	1,992,336	241,639,462	136,951,334	201,775,157	182,864,252	86,432,928	19,758	2,900	36,308,371	1,187,926
Ind. and Ill.	22,184,143	7,987,413	460,795,843	187,070,255	344,497,236	97,460,092	78,020,865	137,759	71,942	43,476,748	1,890,377
Okla. and Kan.	60,805,183	9,378,896	865,799,574	415,222,396	1,311,145,229	109,876,505	48,726,352	56,659	10,434	68,125,325	2,525,447
Tex. and La	81,733,167	5,579,957	636,856,670	435,281,246	1,934,441,119	123,258,451	73,145,391	107,931	145,887	352,028,239	3,019,166
Colo. and Wyo	11,913,125	4,627,512	212,108,809	62,695,223	243,755,929	3,653,539	2,259,346	14,912	40	136,475,995	732,931
California	66,464,969	13,669,007	434,392,494	102,580,454	2,133,784,156	66,940,253	768,032	.....	106,593	571,678,155	1,568,790
Total 1918	326,024,630	50,565,204	3,570,312,963	1,825,380,137	7,321,397,557	851,465,767	505,114,357	559,663	607,968	1,286,710,383	14,556,625
do. 1917	315,131,681	1 14,897,670	2,850,546,123	1,726,768,976	6,513,324,280	753,776,840	481,200,081	539,366	739,425	702,167,243	13,073,829
Increase	10,892,949	....	719,766,340	98,591,161	808,073,277	87,688,927	23,944,276	20,297	2 131,457	584,543,110	1,482,796
Daily avge. 1918	893,218	138,535	9,781,679	5,000,987	20,058,623	2,305,386	1,383,957	1,533	1,666	3,525,234	39,881
do. 1917	863,374	80,966	7,809,716	4,730,874	17,844,724	2,065,142	1,318,336	1,478	2,026	1,923,746	35,819
Increase	29,844	.....	1,971,963	270,113	2,213,899	240,244	65,601	55	2 360	1,601,488	4,062

1 Total of last six months of 1917. 2 Decrease.

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES

Output of Refineries in the United States by Months, 1918

1918	Crude run (bbl)	Oils Purchased and re-run (bbl)	Gasoline (gal)	Kerosene (gal)	Gas and fuel (gal)	Lubricating (gal)	Wax (lb.)	Coke (ton)	Asphalt (ton)	Miscellaneous (gal.)	Losses (bbl.)
January	23,812,587	2,300,434	242,632,044	119,355,184	547,866,248	56,023,425	39,238,858	41,216	54,854	70,995,829	1,078,181
February	23,386,670	2,298,333	234,324,619	121,218,320	510,165,397	58,300,914	35,087,337	42,371	42,033	75,134,088	983,992
March	26,239,662	3,096,872	269,627,968	151,228,007	587,985,804	69,305,331	43,397,019	44,248	56,901	94,865,148	1,097,489
April	26,201,544	3,956,244	293,396,102	153,703,682	578,255,341	71,022,204	40,173,524	45,674	51,242	89,242,012	1,182,020
May	28,510,698	4,112,023	319,391,202	160,590,760	631,586,209	79,380,735	42,544,633	48,864	60,449	88,627,491	1,269,281
June	28,140,479	3,483,270	315,023,443	151,840,232	628,842,033	74,120,996	41,317,794	46,605	50,321	81,110,922	1,282,170
July	29,170,718	5,951,537	332,022,095	156,828,826	638,439,682	79,303,107	41,691,551	48,914	58,433	159,374,139	1,338,304
August	28,534,275	6,376,353	330,335,046	149,678,850	671,113,871	72,892,879	41,829,516	51,759	59,715	163,345,034	1,337,327
September	28,390,431	5,485,747	314,585,959	164,963,798	653,085,050	70,593,079	42,704,894	48,052	49,157	138,201,963	1,236,834
October	29,237,767	5,571,847	314,251,318	164,928,640	661,780,441	72,244,633	43,470,132	48,820	51,878	166,109,867	1,161,545
November	27,411,636	3,857,754	312,968,640	169,278,105	604,403,494	72,178,602	49,642,007	51,393	35,387	75,430,160	1,236,818
December	26,958,157	3,474,880	291,744,165	161,712,713	587,873,987	64,987,842	43,847,092	41,747	37,598	84,273,730	1,352,657
Total	326,024,630	50,565,204	3,570,312,963	1,825,360,137	7,321,397,557	841,465,767	505,114,357	559,663	607,968	1,286,710,383	14,556,625

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES

Output by Sections of the Refineries in the United States for 1919

	Run to the stills		Gasoline (gal)	Kerosene (gal)	Gas and fuel (gal)	Lubricating (gal)	Wax (lb)	Coke (ton)	Asphalt (ton)	Miscellaneous (gal)	Losses (bbl.)
	Crude oil (bbl)	Other oils (bbl)									
East Coast ..	74,869,891	6,509,424	779,698,016	703,112,919	1,226,192,099	280,224,126	186,791,005	248,945	430,135	75,678,218	4,137,640
Penna... ..	20,483,273	2,156,015	270,113,740	190,023,584	169,282,410	180,985,515	87,703,238	18,157	2,115	65,115,629	1,363,835
Ind. and Ill...	29,598,216	9,607,374	571,477,670	216,704,665	480,241,614	102,022,709	69,399,635	137,065	91,309	147,537,937	2,325,185
Okla and Kan.	61,991,730	6,057,548	880,724,011	392,879,976	1,250,048,928	93,207,776	43,782,952	56,843	172	99,214,085	2,727,227
Tex. and La	88,943,946	5,928,807	800,336,848	568,957,294	1,912,251,972	121,223,387	74,459,594	122,268	210,532	365,163,867	3,043,689
Colo. and Wyo	12,700,015	7,351,062	237,713,872	65,691,295	279,701,842	3,481,554	3,070,741	20,181	20	219,311,185	716,819
California..	72,933,052	8,121,786	417,792,940	203,662,431	2,300,339,701	65,614,950	2,028,058		167,602	306,842,859	1,700,831
Total 1919 ..	361,520,153	45,762,616	3,957,855,097	2,341,632,164	7,627,288,566	846,780,017	467,235,223	603,459	901,885	1,278,863,780	16,015,226
do. 1918 .	326,024,630	50,565,204	3,570,312,063	1,825,360,137	7,321,397,537	841,465,767	501,144,357	559,663	607,968	1,286,710,383	14,556,625
do. 1917.	315,131,681	114,897,670	2,850,546,423	1,726,768,976	6,313,324,280	753,776,840	481,200,081	339,366	739,425	703,167,243	13,073,829
Daily avge.1919	990,466	125,278	10,843,444	6,415,430	20,896,681	2,319,891	1,280,097	1,653	2,197	3,503,736	43,857
do. 1918	893,218	138,535	9,781,679	5,000,987	20,058,623	2,305,386	1,383,957	1,533	1,666	3,325,234	39,881
do. 1917	863,374	80,966	7,809,716	4,730,874	17,844,724	2,065,142	1,318,356	1,478	2,026	1,923,746	35,819

1 Total last six months of 1917.

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES

Output by Months of the Refineries in the United States for 1919

1919	Run to the stills		Gasoline (gal)	Kerosene (gal)	Gas and fuel (gal)	Lubricating (gal)	Wax (lb.)	Coke (ton)	Asphalt (ton)	Miscellaneous (Gal)	Losses (bbl)
	Crude oil (bbl)	Other oils (bbl)									
January	26,967,332	3,919,492	303,710,536	158,501,200	589,630,056	68,304,613	44,957,663	59,003	50,074	92,824,236	1,183,767
February	25,232,876	3,997,025	283,518,194	164,191,787	553,853,753	62,503,072	42,704,886	57,200	11,348	88,315,735	1,115,040
March	27,866,775	3,351,821	311,306,755	170,290,980	574,774,156	67,063,995	43,255,128	58,642	50,139	107,880,754	1,176,746
April	27,775,217	4,197,450	319,807,838	188,453,728	588,808,408	70,954,128	42,052,672	46,332	51,329	96,495,501	1,293,543
May	30,267,227	4,720,920	354,472,377	190,345,026	652,166,738	76,442,252	39,503,833	50,998	73,916	100,470,163	1,418,527
June	28,920,764	3,992,009	338,336,985	178,974,221	632,205,805	64,636,153	34,818,104	41,362	73,165	121,500,018	1,315,748
July	31,202,522	3,762,957	342,491,757	205,727,289	638,185,469	67,037,414	38,270,440	47,009	80,205	116,575,092	1,480,984
August	32,362,057	3,713,556	326,846,167	219,502,888	685,702,461	72,920,214	30,939,565	49,742	90,706	110,413,444	1,465,849
September ..	32,601,044	3,216,889	339,582,564	199,244,293	683,409,671	70,236,602	36,638,632	47,476	93,590	109,264,911	1,513,702
October	33,632,968	3,491,094	363,456,747	227,101,346	680,158,446	78,658,410	40,271,266	52,577	105,814	110,616,107	1,403,060
November ..	32,213,754	3,579,314	338,667,570	214,829,925	663,309,514	75,962,212	38,856,628	50,472	105,217	112,870,968	1,362,012
December ..	32,427,617	3,820,089	335,639,587	229,476,468	685,084,686	72,040,862	34,938,526	42,646	82,382	111,935,851	1,286,248
Total	361,520,153	45,762,616	3,957,857,097	2,341,632,164	7,627,288,366	846,760,017	467,235,223	603,459	901,885	1,278,863,780	16,015,226

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES

Output of Refineries in the United States for January, 1920

1920	East Coast (N.Y., Phila and Baltimore)	Pa., N.Y., East Ohio, and W.Va	W Ohio, Ind., Ill., Ky and Tenn.	Oklahoma and Kansas	Texas and Louisiana	Colorado and Wyoming	California	Total	Daily average		
									January, 1920	January, 1919	January, 1918
Crude run (bbl)	6,213,541	1,595,948	3,047,234	5,243,926	7,912,352	1,057,947	5,744,212	30,815,160	994,038	869,914	769,118
Oils purchased and re-run (bbl)	554,619	172,923	455,815	221,012	791,586	446,497	455,805	3,098,347	99,947	126,435	74,204
Gasoline (gal)	68,150,484	20,726,835	47,145,043	73,333,033	75,892,317	18,483,424	32,988,021	336,719,157	10,861,908	9,797,115	7,826,840
Kerosene (gal)	47,668,220	14,254,004	17,271,401	33,645,516	61,356,398	5,211,809	16,349,044	195,956,392	6,321,174	5,112,944	3,850,264
Gas and fuel (gal)	112,467,484	16,214,536	45,313,662	98,611,075	153,041,518	15,994,092	175,912,789	617,555,156	19,921,134	19,020,324	17,673,105
Lubricating (gal)	25,356,041	14,844,405	7,156,526	5,637,684	15,236,740	1,012,572	6,584,667	75,878,635	2,447,698	2,203,375	1,826,562
Wax (lb.)	17,403,142	7,180,534	4,661,652	2,731,154	6,986,015	726,378	319,651	40,008,556	1,290,599	1,451,213	1,265,770
Coke (ton)	12,750	1,376	9,988	3,026	10,821	566	...	38,527	1,243	1,903	1,330
Asphalt (ton)	28,470	409	6,650	...	23,718	...	13,885	73,132	2,359	1,744	1,769
Miscellaneous (gal)	5,313,442	2,475,460	15,380,649	8,177,578	40,506,881	18,983,655	19,196,467	110,104,132	3,551,746	2,978,201	2,290,188
Losses (bbl)	318,614	101,120	214,661	198,497	233,931	76,965	143,934	1,287,722	41,539	38,186	34,780

DEPARTMENT OF THE INTERIOR.　BUREAU OF MINES

Output of Refineries in the United States for February, 1920

1920	East Coast (N.Y.,Phila and Baltimore)	Pa., N.Y., East Ohio, and W. Va.	W. Ohio, Ind., Ill., Ky and Tenn.	Oklahoma and Kansas	Texas and Louisiana	Colorado and Wyoming	California	Total	Daily average		
									February, 1920	February, 1919	February, 1918
Crude run (bbl)	5,635,110	1,455,748	3,073,566	5,117,170	7,526,774	1,167,511	5,232,844	29,208,723	1,007,197	901,074	835,238
Oils purchased and re-run (bbl)	577,922	192,800	548,695	233,149	731,806	519,725	496,977	3,301,074	113,870	142,751	82,083
Gasoline (gal.)	57,902,258	20,025,695	49,678,529	69,871,578	68,810,531	21,943,163	34,356,943	322,588,697	11,123,748	10,125,650	8,352,665
Kerosene (gal.)	43,000,961	13,672,905	19,281,032	31,927,660	62,307,637	8,406,504	15,926,633	194,523,334	6,707,701	5,863,635	4,329,226
Gas and fuel (gal.)	107,359,882	14,741,766	45,537,768	99,054,781	150,788,588	15,829,062	156,373,010	589,684,857	20,333,961	19,780,491	18,220,193
Lubricating (gal.)	24,107,178	13,172,882	8,314,527	6,902,424	13,131,049	1,296,724	7,318,289	74,243,073	2,560,106	2,232,253	2,082,175
Wax (lb.)	16,230,689	6,890,462	5,206,405	2,902,426	7,098,172	1,284,351	208,651	39,821,756	1,373,164	1,525,103	1,253,119
Coke (ton)	13,784	1,682	10,589	2,061	8,647	1,045	......	37,808	1,304	2,043	1,513
Asphalt (ton)	29,743	236	7,219	......	19,497	......	14,025	70,720	2,439	1,477	1,501
Miscellaneous (gal.)	6,511,173	2,076,704	15,134,348	8,443,235	34,036,122	19,381,503	18,372,062	103,955,147	3,584,660	3,161,276	2,683,360
Losses (bbl)	234,456	100,652	218,075	174,286	235,470	84,092	119,473	1,166,504	40,225	39,823	35,143

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES

Output of Refineries in the United States for March, 1920

1920	East Coast (N.Y., Phila and Baltimore)	Pa., N.Y., East Ohio and W. Va	W. Ohio, Ind., Ill., Ky. and Tenn.	Oklahoma and Kansas	Texas and Louisiana	Colorado and Wyoming	California	Total	Daily average		
									March, 1920	March, 1919	March, 1918
Crude Run (bbl)	6,672,610	1,665,225	3,077,308	5,455,185	9,164,122	1,278,171	6,279,383	33,592,004	1,083,616	898,928	846,441
Oils purchased and re-run (bbl.)	441,431	169,222	481,518	137,606	1,011,007	543,154	398,903	3,182,841	102,672	108,123	119,254
Gasoline (gal)	71,066,252	23,371,100	52,873,344	70,991,944	87,323,078	23,059,164	38,432,796	367,137,678	11,843,151	10,042,153	8,697,676
Kerosene (gal,)	40,885,918	13,660,120	16,428,059	33,731,543	58,075,184	8,884,332	19,445,019	191,110,175	6,164,844	5,493,256	4,878,323
Gas and fuel (gal)	129,590,303	14,522,592	42,147,085	102,962,619	199,237,875	16,051,239	182,431,250	686,945,963	22,159,547	18,541,102	18,967,284
Lubricating (gal)	27,370,520	15,265,882	8,471,151	8,331,226	14,488,579	928,137	6,963,478	81,818,973	2,639,322	2,163,355	2,235,753
Wax (lb)	19,592,901	7,224,459	5,586,620	3,720,601	6,510,142	2,049,504	201,894	44,886,121	1,447,939	1,395,327	1,417,968
Coke (ton)	16,989	1,320	10,219	3,009	11,783	1,046		44,366	1,431	1,892	1,427
Asphalt (ton)	36,558	404	7,114		33,996	19,568		97,700	3,152	1,617	1,836
Miscellaneous (gal)	3,867,921	4,484,614	16,129,842	9,304,175	43,800,443	23,732,645	23,467,775	124,767,415	4,025,400	3,480,024	3,060,166
Losses (bbl.)	266,243	101,806	193,469	181,627	298,482	77,984	121,398	1,241,009	40,033	37,960	35,403

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES

Output of Refineries in the United States for April, 1920

1920	East Coast (N.Y., Phila., and Baltimore)	Pa., N.Y., East Ohio, and W. Va	W. Ohio, Ind., Ill., Ky., and Tenn	Oklahoma and Kansas	Texas and Louisiana	Colorado and Wyoming	California	Total	Daily average		
									April, 1920	April, 1919	April, 1918
Crude run (bbl)	7,000,083	1,826,730	2,903,601	5,125,573	8,868,206	1,269,654	5,858,193	32,852,040	1,095,068	825,810	873,385
Oils purchased and re-run (bbl)	205,116	153,549	438,289	182,392	819,081	467,885	473,161	2,829,373	94,312	139,915	131,875
Gasoline (gal.)	67,018,514	24,411,967	47,903,279	69,921,723	85,976,617	22,081,626	38,283,725	355,597,451	11,853,248	10,660,261	9,779,852
Kerosene (gal)	45,583,384	15,150,311	14,164,704	61,319,032	52,274,512	8,254,420	17,521,724	184,469,017	6,148,967	6,115,124	5,123,456
Gas and fuel (gal.)	404,480,674	14,042,192	14,949,583	93,157,122	169,862,504	15,744,288	171,732,122	643,088,785	21,436,293	19,626,947	19,275,178
Lubricating (gal.)	29,615,312	15,891,548	7,497,975	9,615,501	14,951,749	1,072,144	6,923,805	85,568,064	2,852,269	2,365,137	2,367,407
Wax (lb.)	17,621,648	8,428,338	4,427,352	5,350,309	5,036,851	2,137,610	351,285	43,353,393	1,445,113	1,401,756	1,339,117
Coke (ton)	17,030	1,580	9,287	2,783	9,387	525		40,592	1,333	1,544	1,522
Asphalt (ton)	32,525	561	6,306		30,760		16,790	86,942	2,898	1,711	1,708
Miscellaneous (gal)	4,318,770	3,984,383	14,087,369	7,505,936	57,712,353	21,011,578	21,894,551	130,514,940	4,350,498	3,216,517	2,974,734
Losses (bbl)	343,860	116,519	190,551	227,283	381,536	103,334	132,937	1,496,050	49,868	43,118	39,401

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES

Comparative Analysis of Production and Consumption (Years of 1919 and 1918)

(Unit of Gallons)

	Gasoline		Kerosene		Gas and Fuel		Lubricating	
	1919	1918	1919	1918	1919	1918	1919	1918
Income:								
Stocks Dec 31, 1918 and 1917	297,326,983	412,256,833	380,117,829	497,750,082	659,001,357	577,899,112	138,853,574	136,856,348
Production for 1919	3,957,857,097	3,570,312,963	2,341,632,104	1,825,360,137	7,627,288,566	7,321,397,557	846,760,017	841,465,767
Total	4,255,184,080	3,982,569,796	2,721,749,993	2,323,110,219	8,286,289,923	7,899,296,669	985,613,591	978,322,115
Exports	365,883,011	556,422,334	965,415,225	484,613,905 [1]	1,174,166,557 [1]	1,477,085,287	276,051,479	256,300,689
Shipments to our insular possessions	16,217,081	12,209,957	20,272,439	11,830,802	107,630,830	43,986,549	3,860,199	2,615,666
Domestic consumption	3,426,290,557	3,116,610,522	1,396,742,639	1,446,547,683	6,290,368,081	5,719,223,476	568,382,979	580,552,186
Stocks Dec. 31, 1919 and 1918	446,793,431	297,326,983	339,319,690	380,117,829	714,124,455	659,001,357	137,318,934	138,853,574
Total	4,255,184,080	3,982,569,796	2,721,749,993	2,323,110,219	8,286,289,923	7,899,296,669	985,613,591	978,322,115

Figures on exports and shipments are taken from reports of the Bureau of Foreign and Domestic Commerce

1 Includes fuel or bunker oil for vessels engaged in foreign trade   For year 1919 — 14,031,356 bbl.; 1918 — 6,578,141 bbl.

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES

Comparative Analysis of Production and Consumption (First Half of 1919 and 1918)

(Unit of Gallons)

	Gasoline		Kerosene		Gas and fuel		Lubricating	
	1919	1918	1919	1918	1919	1918	1919	1918
Income:								
Stocks Dec 31, 1918 and 1917...	297,326,983	412,256,833	380,117,829	497,750,082	639,001,357	577,899,112	138,853,574	136,855,348
Production, first half 1919	1,911,152,705	1,674,395,440	1,045,746,955	857,939,205	3,591,438,916	3,484,701,032	409,904,213	409,265,625
Total	2,208,479,688	2,086,652,273	1,425,864,784	1,355,689,287	4,230,440,273	4,062,600,144	548,757,787	546,120,973
Outgo:								
Exports	177,798,652	275,373,335	475,290,524	251,965,121	507,347,261	720,294,148	147,695,436	127,404,845
Domestic consumption	9,727,261	6,952,651	10,122,293	6,887,925	58,323,457	2,012,510	1,364,544	1,350,664
Domestic consumption	1,427,057,162	1,535,885,934	687,909,533	670,550,565	2,872,978,918	2,789,588,727	224,313,032	259,049,187
Stocks June 30, 1919 and 1918	593,896,610	418,440,353	252,542,434	426,285,676	811,790,637	550,704,759	175,384,775	158,316,257
Total	2,208,479,688	2,086,652,273	1,425,864,784	1,355,689,287	4,230,440,273	4,062,600,144	548,757,787	646,120,973

Figures on exports and shipments are taken from reports of the Bureau of Foreign and Domestic Commerce.

1 Includes fuel or bunker oil for vessels engaged in foreign trade. 1919 — 5,053,957 bbl.; 1918 — 2,975,106 bbl.

DEPARTMENT OF THE INTERIOR. BUREAU OF MINES

Comparative Analysis of Production and Consumption (First Nine Months of 1919 and 1918)

(Unit of Gallons)

	Gasoline		Kerosene		Gas and fuel		Lubricating	
	1919	1918	1919	1918	1919	1918	1919	1918
Income:								
Stocks Dec. 31, 1918 and 1917.........	297,326,893	412,256,833	380,117,829	497,750,082	659,001,337	577,899,112	138,853,574	136,855,348
Production, nine months 1919	2,920,073,193	2,651,348,540	1,670,221,425	1,329,410,679	6,598,736,520	5,467,339,635	620,098,533	632,054,690
Total	3,217,400,176	3,063,605,373	2,050,339,254	1,827,160,761	7,257,737,877	6,045,238,747	758,952,107	768,910,038
Outgo:								
Exports	268,166,964	420,042,281	705,187,835	357,319,920	780,031,398 [1]	1,157,131,704 [1]	207,286,353	193,455,183
Shipments to our insular possessions ..	12,889,050	10,017,080	14,668,192	10,233,006	87,933,207	22,056,313	3,062,113	1,949,014
Domestic consumption	2,565,218,743	2,363,773,289	1,018,640,170	1,022,976,928	5,527,637,887	4,282,642,961	389,636,571	426,080,285
Stocks Sept. 30, 1919 and 1918 . ..	371,125,419	269,772,723	311,843,057	436,628,907	862,135,385	583,407,769	158,967,070	147,425,556
Total........	3,217,400,176	3,063,605,373	2,050,339,254	1,827,160,761	7,257,737,877	6,045,238,747	758,952,107	768,910,038

Figures on exports and shipments are taken from reports of the Bureau of Foreign and Domestic Commerce.

1 Includes fuel or bunker oil for vessels engaged in foreign trade. Nine months 1919 — 8,823,959 bbl., 1918 — 4,785,086 bbl.

Comparative Analysis of Production and Consumption (First Quarter 1918, 1919, and 1920)

(Unit of Gallons)

Income:	Gasoline			Kerosene		
	1920	1919	1918	1920	1919	1918
Stocks, January 1	446,793,431	297,326,983	746,584,631	339,319,690	380,117,829	497,750,082
Production	1,026,445,532	898,535,505	746,584,631	581,589,901	492,973,977	391,804,511
Total	1,473,238,963	1,195,862,488	1,158,841,464	920,909,591	873,091,806	889,554,593
Outgo:						
Exports	109,610,676	96,639,064	123,470,462	233,782,442	184,740,900	136,526,782
Shipments to insular possessions	3,190,434	3,048,527	3,389,345	3,899,876	4,548,619	2,583,213
Domestic consumption	734,044,807	550,112,468	505,599,271	348,610,156	389,124,664	393,864,058
Stocks, March 31	626,393,046	546,062,429	526,382,386	334,617,117	294,677,623	356,580,540
Total	1,473,238,963	1,195,862,488	1,158,841,464	920,909,591	873,091,806	889,554,593

Income:	Gas and fuel			Lubricating		
	1920	1919	1918	1920	1919	1918
Stocks, January 1	714,124,455	659,001,357	577,899,112	137,318,934	138,853,574	136,855,348
Production	1,894,185,976	1,718,257,965	1,646,017,449	231,940,681	197,871,680	184,232,690
Total	2,608,310,431	2,377,259,322	2,223,916,561	369,259,615	336,725,254	321,088,038
Outgo:						
Exports[1]	389,020,315	232,970,028	351,051,012	100,450,227	72,081,945	62,106,421
Shipments to insular possessions	25,801,407	26,250,840	494,554	1,567,046	556,588	557,948
Domestic consumption	1,613,305,851	1,368,970,648	1,388,923,268	136,602,745	98,591,467	111,851,271
Stocks, March 31	580,182,858	749,067,806	483,447,727	130,630,597	165,495,254	146,572,398
Total	2,608,310,431	2,377,259,322	2,223,916,561	369,259,615	336,725,254	321,088,038

Figures on exports and shipments are taken from reports of the Bureau of Foreign and Domestic Commerce

[1] Includes fuel or bunker oil for vessels engaged in foreign trade.   1918 — 1,357,044 bbl.   1919 — 2,017,955 bbl.   1920 — 4,999,676 bbl.

APPENDIX

A census of the petroleum refineries in the United States on January 1, 1920, gives a total of 373 completed refineries with a daily capacity of 1,530,565 barrels; this compared with December report shows 81 refineries with a daily capacity of 174,210 barrels shut down for various reasons. Also, this census gives 99 refineries, daily capacity of 263,500 barrels in the course of construction; by August 1 the new refineries were expected to be completed. Texas leads in new construction with a total of 50 plants, daily capacity of 141,400 barrels; with Oklahoma standing second, 17 plants, daily capacity 22,850 barrels.

In 1919 the United States Geological Survey reports the production of petroleum as 377,719,000 barrels; the Bureau of Foreign and Domestic Commerce reports the import of 52,746,567 barrels, making a total of 430,465,567 barrels, or a daily average of 1,179,358 barrels, which compared with daily capacity of the refineries operating at the end of December, 1919, indicates a surplus capacity of 177,007 barrels daily over the production and importation of crude oil during 1919. If all completed and building refineries as shown by the census of January were operating in August, 1920, the potential surplus capacity over the supply of petroleum would be 614,707 barrels daily.

The exports of crude oil during 1919 were 5,925,586 barrels, or a daily average of 16,234 barrels.

The 430,465,567 barrels of crude petroleum that were produced and imported during the year 1919 are accounted for as follows: 5,925,586 barrels were exported, 328,879 barrels were shipped to our insular possessions and the refineries accounted for 361,520,153 barrels, making a total of 367,774,618 barrels of oil. This leaves a balance of 62,690,949 barrels that were consumed in the natural state.

Of the 52,746,567 barrels of petroleum that were imported during the year, 30,828,264 barrels of Mexican crude were run by the refineries, who in addition used 1,446,326 barrels of Mexican tops.

Gasoline production increased 10 per cent over that of 1918, October being the high month in production and January the low month. Stocks indicate the seasonal demand for this product; the largest stocks were on hand at the refineries at the end of May and the smallest stocks at the close of January and October. Stocks during the year increased from 297,326,983 gallons to 446,793,431 gallons. Exports decreased about 190,000,000 gallons during the year, while the domestic consumption increased 309,000,000 gallons.

Kerosene consistently increased in production since August, 1918, and the 1919 increase amounts to 28 per cent over the production for 1918, the largest monthly production occurring in the month of December, 1919, the low month being January of that year. Stocks

Production and

(Unit of

1917

	January	February	March	April	May
Stocks, first of month . . .	345,613,355	.	No data	available	. .
Production	203,618,724	184,602,595	220,523,571	228,945,164	238,816,209
Imports	2,689,337	. . . .	2,500	60,272	5,350,030
Total	. . . .	. . . . . .	. . . .	. . . . . .	. . . . . .
Exports	38,065,884	21,908,056	24,606,324	35,576,852	46,324,757
Shipments to insular possessions	708,812	1,677,473	334,107	1,826,643	1,405,144
Domestic consumption . .	.		No data	available	. .
Stocks, end of month.		. . .	No data	available	. . . . . .
Total	. . . . .	. . . .	. . .	.	. . . . . .

1918

	January	February	March	April	May
Stocks, first of month . . .	412,256,833	473,165,166	523,727,009	526,382,386	509,197,134
Production . . .	242,632,044	234,324,619	269,627,968	293,396,162	319,391,202
Imports	5,034,955	. . . . .	5	2,631,109	1,008,000
Total	659,923,832	707,489,785	793,354,982	822,409,657	829,596,336
Exports	41,683,642	35,396,038	46,390,782	46,857,293	56,748,164
Shipments to insular possessions	1,107,355	1,162,361	1,119,629	1,203,819	686,090
Domestic consumption . .	143,967,669	147,204,377	219,462,185	265,151,411	311,524,603
Stocks, end of month .	473,165,166	523,727,009	526,382,386	509,197,134	460,637,479
Total	659,923,832	707,489,785	793,354,982	822,409,657	829,596,336

Consumption of Gasoline.

(Gallon)

1917

June	July	August	September	October	November	December	Total
	383,415,992	315,199,195	298,518,699	287,758,562	320,203,770	360,241,135	345,613,355
233,671,746	241,145,292	254,464,491	256,132,050	271,891,231	264,888,709	248,846,638	2,850,546,423
	84	57	6,016	36	. .	2,386,287	10,491,619
	627,561,368	599,663,743	554,686,765	559,619,832	585,092,479	611,474,060	3,538,128,247
53,291,?39	22,076,056	30,598,219	20,079,759	31,240,762	56,996,017	35,355,977	416,249,063
1,882,426	655,781	2,038,202	1,372,593	1,155,929	1,151,417	697,639	14,918,100
	259,630,336	268,478,623	245,475,851	207,049,371	166,703,910	163,183,611	2,694,704,251
383,415,992	345,199,195	298,548,699	287,758,562	320,203,770	360,241,135	412,256,832	412,256,833
	627,561,368	599,663,743	554,686,765	559,649,832	585,092,479	611,474,060	3,538,128,247

1918

June	July	August	September	October	November	December	Total
460,637,479	118,440,353	349,928,604	285,416,538	269,772,723	250,328,329	270,072,011	360,241,135
315,023,445	332,022,095	330,335,046	314,595,959	314,251,318	312,968,640	291,744,165	3,570,312,963
3,350		3,352	1,867	3,040,712		1,176,000	12,899,350
775,664,274	750,462,448	680,267,002	600,004,364	587,064,753	563,296,969	562,992,476	3,913,453,448
48,297,416	47,412,552	55,920,752	44,540,511	37,915,924	47,667,016	54,278,755	559,125,330
1,670,897	531,737	1,240,014	1,295,148	633,943	288,698	1,270,236	12,209,957
307,255,608	352,589,555	337,659,668	284,435,982	298,186,557	245,269,244	210,116,502	3,074,791,178
418,440,353	349,928,604	285,416,538	269,772,723	250,328,329	270,072,011	297,326,983	297,326,983
775,664,274	750,462,448	680,267,002	600,044,364	587,064,753	563,296,969	562,992,476	3,913,453,448

Production and

(Unit of

1919

	January	February	March	April	May
Stocks, first of month........	297,326,983	383,212,692	458,149,187	546,062,429	593,616,170
Production.................	303,710,556	283,518,194	311,306,755	319,807,838	354,472,377
Imports	322	6,042,410	6,186	10	672,555
Total............... ..	601,037,861	672,773,296	769,762,128	865,870,277	948,761,102
Exports	47,614,206	26,650,586	22,374,272	26,540,466	23,111,789
Shipments to insular possessions	954,086	1,773,331	321,110	2,273,026	3,335,977
Domestic consumption.	169,256,877	185,900,192	201,004,317	243,440,615	328,277,648
Stocks, end of month	383,212,692	458,149,187	546,062,429	593,616,170	594,035,688
Total	601,037,861	672,773,296	769,762,128	865,870,277	948,761,102

1920

	January	February	March	April	May
Stocks, first of month........	446,793,431	515,934,364	562,996,189	626,393,046	....
Production.................	336,719,157	322,588,697	367,137,678	355,597,151	....
Imports	2,016,000	6,555,990	3,474	3,361,560	....
Total.................	785,528,588	845,079,051	930,137,641	985,352,057	....
Exports	30,351,871	32,181,444	47,077,361	43,431,948	....
Shipments to insular possessions	1,037,835	1,505,901	646,695	1,366,315	....
Domestic consumption	238,204,518	248,395,211	256,020,539	297,001,120	....
Stocks, end of month	515,934,364	562,996,189	626,393,046	643,552,641	....
Total.................	785,528,588	845,079,051	930,137,641	985,352,057	....

sumption of Gasol..

(Gallons)

June	July	August	September	October	November	December	Total
591,035,688	593,896,610	514,919,358	434,531,446	371,225,419	354,160,071	378,133,185	297,326,983
338,336,985	342,491,757	326,846,167	339,582,561	363,456,747	338,667,570	335,659,587	3,957,857,097
61,142	1,263,929	8,099	1,267,565	...		1,476,208	871,143	11,670,169
932,434,115	937,652,296	841,773,624	775,381,575	731,582,166	694,303,849	714,664,215	4,266,854,219
31,507,333	24,301,168	29,327,003	36,737,141	39,919,358	31,001,477	28,916,689	365,883,011
1,069,734	837,612	1,430,901	893,273	2,073,028	546,138	708,865	16,217,081
305,960,438	397,591,158	376,484,274	366,625,742	338,429,709	284,620,049	238,245,230	3,437,960,726
593,896,610	514,919,358	434,531,446	371,125,419	351,160,071	378,133,185	446,793,431	446,793,431
932,434,115	937,652,296	841,773,624	775,381,575	731,582,166	694,303,849	714,664,215	4,266,854,219

of this oil declined from a high point in October, 1917, to the lowest stock in May, 1919; since this time there was an increase to the highest point of the past year (1919) in November. Four hundred eighty million gallons more kerosene were exported during 1919 than in 1918, and 8,000,000 gallons were shipped to our insular possessions in excess of the shipments during 1918, but domestic consumption decreased by 50,000,000 gallons.

Gas and fuel oil increased in production during the year by 4 per cent; March had the smallest monthly production, with August and December credited with largest productions. Stocks of this product increased steadily from a low reserve at the refineries at the end of January, 1919, to a large stock in September; since that date stocks declined rapidly. Exports of gas and fuel oils decreased 303,000,000 gallons, but shipments to our insular possessions increased by 63,000,000 and 571,000,000 gallons is the increase for domestic consumption. The use of bunker oil for vessels engaged in foreign trade, for 1919, increased 114 per cent over the year of 1918.

Lubricating oils for the year maintained a steady production throughout the year. Stocks were the largest in June; the end of December shows the lowest stock of the year.

PRODUCTION OF GASOLINE FROM NATURAL GAS

Production Statistics [1]

The marketed production of gasoline recovered from natural gas sold in the United States during the years 1911 to 1917 is shown in Table 1 following.

Table I. -- *Gasoline from Natural Gas Marketed in the United States*, 1911–1917 [1]

1911

State	Number of operators	Plants		Gasoline produced			Gas used		Average yield in gasoline per M cubic feet
		Number	Daily capacity	Quantity	Value	Price per gallon	Estimated quantity	Value	
			Gallons	*Gallons*		*Cents*	*Cubic feet*		*Gallons*
West Virginia	47	72	16,819	3,660,165	$262,661	7 18	1,252,900,600	$76,074	2 92
Ohio	26	39	6,454	1,678,985	118,161	7 04	469,672,000	37,574	3 57
Pennsylvania	43	50	5,669	1,467,043	109,649	7 17	526,152,663	52,615	2 79
Oklahoma	8	8	1,800	388,058	20,975	5 40	144,629,000	4,378	2 68
California									
Colorado									
Illinois	8	7	3,358	231,588[2]	20,258	8 75	82,343,000	6,320	2 81
New York									
Kentucky									
	132	176	37,100	7,425,839	531,704	7 16	2,475,697,263	176,961	3.00

[1] Figures for 1911 to 1916 from Mineral Resources of United States for 1916, U S Geol Survey, 1917, pp. 648 649, figures for 1917 supplied by U S Geol Survey
[2] Includes gasoline produced in Kentucky which came from natural condensation in gas mains.

1912

State	Number of operators	Plants		Gasoline produced			Gas used		Average yield
		Number	Daily capacity	Quantity	Value	Price per gallon	Estimated quantity	Value	
			Gallons	*Gallons*		*Cents*	*Cubic feet*		*Gallons*
West Virginia	66	97	22,366	5,318,136	$513,116	9 6	1,972,882,212	$163,749	2 8
Pennsylvania	69	83	10,524	2,041,109	217,016	10 6	722,730,117	62,010	2 8
Ohio	25	43	7,791	1,718,719	173,421	10 1	576,123,700	46,090	2 98
Oklahoma	11	13	11,910	1,575,644	99,626	6 3	701,044,300	24,901	2 25
California	7	7	6,669	1,010,695	112,502	10 8	600,743,000	25,573	1 7
Illinois	4	4							
Colorado	2	2	2,008	386,876[1]	41,795	10 8	114,273,000	9,662	3.4
New York	1	1							
Kentucky	1								
	186	250	61,268	12,081,179	1,157,476	9 6	4,687,796,329	331,985	2 6

[1] Dykema, Absorption Process, Bureau of Mines Bulletin 76.

Table I. — *Gasoline from Natural Gas Marketed in the United States, etc.*
— Continued

1913

State	Number of operators	Plants		Gasoline produced			Gas used		Average yield in gasolene per M cubic feet
		Number	Daily capacity	Quantity	Value	Price per gallon	Estimated quantity	Value	
West Virginia	63	115	31,930	7,662,493	$807,406	10 54	2,981,119,000	$181,337	2 57
Oklahoma .	19	40	61,633	6,462,968	577,944	8 94	2,152,503,000	82,742	3 00
Pennsylvania	100	113	22,207	3,680,096	405,186	11 01	1,372,056,000	114,783	2 68
California...	12	14	21,135	3,460,747	376,227	10 87	2,436,445,000	106,539	1 42
Ohio.........	25	41	8,142	2,072,687	212,404	10 25	741,226,000	63,233	2 79
Illinois.......	6	12							
Colorado ...	2	2							
New York .	3	3	7,368	721,826[1]	79,276	10 98	203,092,500	17,590	3 55
Kansas	1	1							
Kentucky...	1								
	232	341	152,415	24,060,817	2,458,443	10 22	9,889,441,500	566,224	2 43

1914

State	Number of operators	Plants		Gasoline produced			Gas used		Average yield
Oklahoma ..	35	58	74,793	17,277,555	$113,059	6 44	5,738,549,000	$273,940	3 01
West Virginia	65	121	31,460	9,278,108	694,899	7 45	3,005,292,000	172,396	2 58
California .	17	19	32,360	7,581,309	633,517	8 36	5,129,709,000	197,066	1 48
Pennsylvania	96	119	21,456	4,611,738	359,402	7.79	1,560,664,000	125,690	2 89
Ohio	25	47	9,319	2,410,171	184,097	7 54	852,277,000	68,935	2 86
Illinois.......	7	14	5,300	1,164,178	100,331	8 62	462,321,000	43,017	2 52
Kansas ..	3	3							
New York ..	3	3	1,665	299,573[1]	23,604	7 88	146,345,000	8,862	2 08
Colorado ...	2	2							
Kentucky ..	1								
	254	386	179,353	12,652,632	3,105,909	7 28	16,894,557,000	889,906	2 43

1915

State	Number of operators	Plants		Gasoline produced			Gas used		Average yield
Oklahoma ...	36	63	111,463	31,665,991	$2361,029	7 46	8,791,881,000	$435,512	3 60
California ..	18	20	40,755	12,835,126	975,397	7 60	8,006,888,000	288,669	1 60
West Virginia [2]	66	114	34,422	10,853,608	927,079	8 54	3,526,575,000	150,918	2 30
Pennsylvania [2]	116	139	22,745	5,898,597	569,873	9 66	1,838,034,000	186,325	2 73
Ohio.........	23	50	8,995	2,198,715	167,138	7 60	785,044,000	77,767	2 80
Illinois	8	16	8,500	1,035,204	80,049	7 73	451,663,000	3,405	2 29
Texas	1	1							
New York ..	4	4							
Louisiana	2	2	5,447	877,424	70,258	8 01	664,309,000	28,959	1 32
Kansas	3	2							
Colorado.....	2	2							
Kentucky [2]..	2	1							
	287	414	232,336	65,364,665	5,150,823	7.88	24,064,391,000	1,202,555	2 57

[1] Includes gasoline produced in Kentucky which came from natural condensation in gas mains.
[2] Includes gasoline resulting from natural condensation in gas mains.

Table I. — *Gasoline from Natural Gas Marketed in the United States, etc.*
— Continued

1916

State	Number of operators	Plants		Gasoline produced			Estimated quantity of gas treated	Average yield of gasoline per thousand cubic feet of gas
		Number	Daily capacity	Quantity	Value	Price per gallon		
			Gallons	*Gallons*		*Cents*	*M cubic ft*	*Gallons*
Oklahoma	77	116	233,077	48,359,602	$5,865,145	12 13	24,749,154	1 954
West Virginia	105	147	98,659	18,765,056	3,025,293	16 12	104,664,536	179
California	28	26	54,060	17,158,754	2,293,822	13 37	24,826,354	691
Pennsylvania	167	195	46,487	9,714,926	1,726,173	17 77	38,490,021	252
Ohio	40	55	18,391	2,638,571	470,804	17 84	5,435,759	485
Illinois	17	32	12,070	2,260,288	262,664	11 58	1,338,594	1 688
Louisiana	7	7	10,661	2,113,159	269,564	12 76	907,153	2 329
Texas	3	4	6,688	1,292,811	201,023	15 55	948,485	1 363
Kentucky	5	5	11,300	725,467	141,347	19 48	5,614,613	129
Kansas	4	3	3,030	215,000	35,030	16 29	1,626,635	132
New York Colorado	7	6	1,025	219,055	40,283	16 17	102,819	2 422
	460	596	495,448	103,492,689	14,331,148	13 85	208,705,023	496

1917

State	Number of operators	Plants		Gasoline produced			Estimated quantity of gas treated	Average yield
		Number	Daily capacity	Quantity	Value	Price per gallon		
Oklahoma	167	234	192,436	115,123,424	21,541,905	18 71	84,719,944	1 359
West Virginia	128	188	135,663	32,608,647	6,511,813	19 93	167,771,351	195
California	15	19	99,761	28,817,604	4,438,022	15 40	45,351,247	635
Pennsylvania	287	251	59,164	13,826,250	2,778,098	20 01	49,487,056	279
Texas	40	41	32,550	6,920,405	1,119,441	16 64	12,677,216	546
Ohio	49	61	25,437	5,439,560	1,051,376	19 33	30,062,141	181
Louisiana	15	20	20,148	4,979,754	844,747	16 36	2,233,511	2 229
Illinois	33	55	17,392	4,934,009	866,033	17 55	2,685,895	1 837
Kentucky	5	5	13,400	3,818,209	763,186	19 99	21,915,946	153
Kansas	4	6	4,642	1,174,980	244,219	20 53	9,315,339	.126
New York Colorado	7	6	2,122	181,262	33,116	18 27	68,154	2 659
	750	886	902,385	217,884,104	40,188,956	18 45	429,287,797	508

The production of gasoline from natural gas by compression and vacuum methods and by the absorption method for the years 1916 and 1917 is shown in Tables II and III. The tables show that the quantity of gas treated in 1917 was more than double that of 1916, and that most of this increase was from gas treated in absorption plants.

Table II. — *Production of Gasoline from Natural Gas in 1916 by Principal Methods of Manufacture* [1]

Gasoline produced by compression and by vacuum methods

State	Plants		Gasoline produced			Gas used	
	Num-ber	Daily capacity	Quantity	Value	Price per gallon	Estimated quantity	Average yield in gasolene per M cubic feet
		Gallons	*Gallons*		*Cents*	*M cubic ft.*	*Gallons*
Oklahoma .	104	215,377	45,827,325	$5,471,307	11 94	14,018,757	3 269
West Virginia	133	39,276	9,289,624	1,642,031	17 67	3,550,523	2 616
Pennsylvania	185	30,287	6,722,370	1,216,717	18 10	2,693,215	2 96
Louisiana .	7	10,661	213,159	269,564	12 76	907,153	2 329
Texas.......	4	6,688	1,292,811	201,023	15 55	948,485	1 363
New York	5	} 1,025	249,055	40,283	16 17	102,819	2 422
Colorado.....	1						
California ...	24						
Ohio........	53						
Illinois	29	} 72,251	19,428,413	2,652,776	13 65	14,492,463	.... .
Kentucky ..	3						
Kansas	2						
	550	375,565	84,922,787	11,193,701	13 53	36,713,415	.. .

Gasoline produced by absorption method [2]

State	Num-ber	Daily capacity	Quantity	Value	Price per gallon	Estimated quantity	Average yield
West Virginia	14	59,383	9,475,432	1,383,262	14 60	101,114,013	0 094
Pennsylvania	10	16,200	2,992,556	509,456	17 02	35,797,406	084
Oklahoma....	12	17,700	2,532,277	393,838	15 55	10,730,697	235
California.....	2	} 26,600	3,569,637	550,891	15 43	24,349,492	.....
Kentucky....	2						
Illinois	3						
Ohio.........	2						
Kansas	1						
	46	119,883	18,569,902	2,837,447	15 28	171,991,608 ₄	.. .
Grand total	596	495,448	103,492,689	14,331,148	13.85	208,705,023	.496

[1] Mineral Resources of United States for 1916, U. S. Geol. Survey, 1917, pt. 2, p. 650.

[2] Includes drips.

Table III. — *Production of Gasoline from Natural Gas in 1917 by Principal Methods of Manufacture* [1]

Gasoline produced by compression and by vacuum pumps

State	Plants		Gasoline produced			Gas used	
	Number	Daily capacity	Quantity	Value	Price per gallon	Estimated volume	Average yield of gasolene per M cubic feet
		Gallons	*Gallons*		*Cents*	*M cubic ft.*	*Gallons*
Oklahoma	207	156,632	108,728,213	$20,321,067	18 68	36,399,280	2.987
California	40	82,092	23,478,521	3,637,827	15 49	27,477,443	854
West Virginia	159	44,318	12,276,784	2,211,494	18 01	4,845,648	2 534
Pennsylvania	234	32,564	9,011,199	1,792,430	19 89	3,572,356	2 522
Louisiana	18	17,915	4,459,920	719,758	16 14	1,558,346	2 862
Illinois	54	15,392	4,268,158	756,344	17 72	2,020,014	2 113
Texas	8	10,900	3,942,337	664,543	16 86	2,666,983	1 478
Ohio	54	8,337	2,331,498	423,106	18 15	836,639	2.787
New York	5						
Kansas	1	3,322	369,925	70,361	19 02	150,784	2 453
Kentucky	3						
Colorado	1						
	784	671,502	168,866,555	30,596,930	18 12	79,527,523	2.123

[1] Figures supplied by United States Geological Survey.

Gasoline produced by absorption [1]

State	Number	*Gallons*	*Gallons*		*Cents*	*M cubic ft.*	*Gallons*
West Virginia	29	91,315	20,391,863	$4,300,319	21 09	162,925,703	0 125
Oklahoma	27	35,804	6,395,211	1,220,838	19 09	48,320,661	132
California	9	17,669	5,339,083	800,195	14 99	17,873,804	299
Pennsylvania	17	26,600	4,815,051	985,668	20 47	45,914,700	.105
Kentucky [1]	2	13,000 [2]	3,725,893	745,210	20 00	24,871,590	150
Ohio	7	16,800	3,108,062	628,270	20 21	29,225,502	.106
Texas [3]	3	21,650	2,978,068	484,898	16 28	10,010,233	298
Kansas	5	3,842	1,071,633	220,550	20 58	9,274,289	.116
Illinois [1]	1	2,000	665,851	109,689	16 47	665,851	.000
Louisiana [1]	2	2,203	519,834	94,989	18 27	675,165	.770
New York [4]	...	...	7,000	1,400	20 00	2,776	....
Colorado		..	.....	....		. ...	....
	102	230,883	49,017,549	9,592,026	19 57	349,760,274	140
Grand total	886	902,385	217,884,104	40,188,956	18 45	429,287,797	.508

[1] Includes drip gasolene.
[2] Includes gasolene produced in Kentucky from West Virginia gas.
[3] Includes some gasolene produced by compression.
[4] Drips only.

DEVELOPMENT OF NATURAL GAS INDUSTRY

Allen and **Burrell** [1] summarize developments in the natural gas and artificial oil-gas industries, leading up to the compression processes for recovering valuable products from natural gas and demonstrate the feasibility of manufacturing in large quantity liquid gases from natural gas for industrial application.

The Development of Gas Liquefaction by Pressure (*Ibid.*)

In the early seventies, **J. J. Coleman** [2] successfully liquefied by pressure and cold the gases made by cracking the shale oils of Scotland.

By the process of **Blau,**[3] **Pintsch,**[4] **Gray,**[5] **Hastings-Brink,**[6] the **Swiss Liquid Gas Co.,**[7] **Schneider,**[8] **Williams,**[9] **Wolf,**[10] **Wolski,** [11] and others gas is made by cracking oils in hot retorts. The gas is then washed and compressed into steel cylinders capable of safely withstanding the pressures developed. Several of these processes for manufacturing gases are commercially successful. They all entail the necessity, however, of first manufacturing the gases and then washing them.

The properties of the better known and more widely used illuminating gases are given below.

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[1] Bureau of Mines Technical Paper 10 (1912), Liquefied Products from Natural Gas.

[2] An apparatus for the continuous liquefaction of volatile gases generated from the distillation of bituminous shale, Chem. News, vol. 39, February 28, 1879, p. 87; Mechanical refrigeration, vol. 2; reviewed in Sci. Am. vol. 104, 1911, p. 27, and in Oil and Gas Jour. vol. 9, June 1, 1911, p. 4.

[3] Herstellung eines Leuchtgases aus Destillatgasen, German patent 158,198; Zeitschr. für angew. Chem. 1905, p. 671; Blaugas, Seifens. Zeit. 1907, p. 804; German patent (1905), 175,846: Kruger, F., Blau Gas, Chem. Abs. vol. 2, 1908, p. 3402.

[4] Butterfield, W. J. A., Gas manufacture, 1907, vol. 1, pp. 230–231.

[5] Gray, J. L., Apparatus for recovering light oils from natural gas, U. S. Pat. 933,976, 1909.

[6] Hastings, D., and Brink, A. W., Cooling gas and obtaining gasoline, U. S. Pat. 883,640 (March 31, 1908); Chem. Abs. 1908, 2447.

[7] Mansfield, R. E., Manufacture of liquid illuminating gas in Switzerland, Chem. Eng. vol. 10, p. 122; Chem. Abs. 1910, 102.-

[8] Schneider, W. P., Gas-liquefying apparatus for demonstration purposes U. S. Pat. 984,030 (February 14, 1911); Chem. Abs. 1911, 1353.

[9] Williams, O. H. G., Liquid hydrocarbons from compressed petroleum gas, J. S. C. I., 1884, 437.

[10] Wolf, L., Liquefied oil gas, Chem. Abs., 1911, 372.

[11] Wolski, ——, Liquefying natural gas by the Linde process, Petroleum Rev. vol. 13, p. 428.

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Properties of Certain Manufactured Gases

Name of gas	Specific gravity (air = 1)	Heat value per cubic foot (0° C and 760 nam. pressure)	Candle-power (British) burning 5 cu. ft. per hour	Unsatu-rated hydro-carbons	Saturated hydro-carbons	Hydrogen
		B.t.u.		Per cent	Per cent	Per cent
Pintsch gas [1] ...	. .	1,500 [2]	45–50	35 65	45 37	12 44
Coal gas [3] ..		630	16	8 0	34 0	47 0
Acetylene [4] . .		1,555	150	.....	.....	. ...
Carbureted water gas [5]			22	12 83	14 78	35 17
Uncarbureted water gas [6]	.		. .	....	0 10	51 89
Ordirary natural gas [7]	64	1,189		.....	99 00	. ...
Liquid natural gas [8]	1 25	1,800–3,300 [9]	45–50	.	99 00	. ...
Manufactured oil gas [9] .	494	633	23	5 85	40 80	39 49

Name of gas	Carbon monoxide	Carbon dioxide	Oxygen	Nitrogen	Explosive limit	
					High	Low
	Per cent	Per cent	Per cent	Per cent		
Pintsch gas [1]	0 60	0 74	2 00	3 00	...	...
Coal gas [3]	9 0	1 1	0 0	2 3	7.1	19 0
Acetylene [4]	....	....	....	. .	3 0	81
Carbureted water gas [5]	33 92	1 54	0 0	1 76	...	....
Uncarbureted water gas [6] .. .	40 08	4 80	. .	3 13	...	...
Ordinary natural gas [7]	. . ..	....	. . .		5 5	12.0
Liquid natural gas [8]	. .	....	....	.	3 0	7 0
Manufactured oil gas [10]	4 50	2 75	0 85	6 01	...	...

[1] Hills, H. F., Gas and gas fittings, 1902, p. 52.
[2] Approximate
[3] Burrell, G. A., Average result of several analyses of coal gas.
[4] Butterfield, W. J. A., The Chemistry of gas manufacture, 1898, p 393.
[5] Butterfield, W. J. A., The Chemistry of gas manufacture, 1907, vol. 1, p 224.
[6] Lewes, V. B., Liquid and gaseous fuels, 1907, p. 220.
[7] Burrell, G. A., Average results of several analyses of West Virginia and western Pennsylvania gases.
[8] Burrell, G. A.
[9] Calculated.
[0] Allen, I. C., Average results of several analyses of manufactured petroleum gas used on the Pacific coast.

The illuminating values given above are those of the ordinary naked flame, without a mantle. How greatly a mantle increases the light is shown in the following table.[1]

Comparative Illuminating Power of Gas Burners

Flat flame, burning 5 cubic feet per hour	Burner equipped with mantle, burning 5 cubic feet per hour
British candle-power	*British candle-power*
23.1	117.3
17.9	90.3
16.2	87.9
14.6	84.4
13.5	81.9

According to **A. C. Humphreys,**[2] "The use of mantles in the Pintsch system increased the lighting effect about four times, and with the same storage capacity the length of period between fillings was increased 60 per cent."

Acetylene has been burned with increased efficiency in mantles but because of the high luminosity and whiteness of the flame itself and because of obstacles yet to be overcome in using mantles the use of mantles with acetylene has not been generally adopted.[2]

According to tests conducted by **Drs. F. Schniewind, Chas E. Chandler, E. G. Love** and **H. Schweitzer**[3] Blau gas has a specific gravity of 0.940, a heating value of 1731 B.T.U. and an illuminating value, when burned in an inverted mantle, of 108 standard candles. It is further stated that 2.52 kilograms of oil will produce 1 kilogram of the gas.

Early Attempts to Liquefy Natural Gas. — The liquefaction of natural-gas products was early recognized as of possible commercial importance.

Pasenmeyer[4] and others procured gasoline in commercial quantities near Titusville, Pa., in 1904, by collecting the condensation in the gas mains. The yield of gasoline so obtained was further increased in 1905 by chilling the pipes with cold water, and from 1905 to 1909 the yield was still further increased by the establishment of small, low-pressure, single-stage compressing plants. In the last few years the industry has made remarkable strides.

[1] **Hills, H. F.,** Gas and gas fittings, 1902, p. 106.

[2] Lectures on illuminating engineering, delivered at the Johns Hopkins University, October and November, 1910, under the joint auspices of the university, and the Illuminating Society, 1911, p. 208.

[3] Prospectus of the Blau Gas Company, pp. 42–43.

[4] Taylor, Frank H., Early history of utilization of gasoline from natural gas, Oil City Derrick, May 6, 1911, p. 9; Oil and Gas Jour. vol. 9, May 11, 1911, p. 20; The gasoline from natural gas industry, Oil and Gas Jour. vol. 9, March 2, 1911, pp. 2–6; Petroleum, March 17, 1911, vol. 6, p. 896.

Up to the last two years the general practice in the manufacture of liquid natural gas was to make the product by compression of the gas in single-stage compressors operated at a pressure of 150 to 300 pounds per square inch. The one product thus obtained, so-called "natural gasoline," was run into a tank and "weathered." The weathering consisted in allowing the lighter portions to volatilize spontaneously and escape into the open air until such time as the boiling away of the liquid had practically ceased. Thus the process involved a loss of 25 to 50 per cent, or even more. This loss was an absolute waste not only of power and of cost of operating the engines and compressors but of the product itself.

Later Improvements. — The next step in the industry was to pass the waste gases (of which only the small quantity used for power had been utilized) from the single-stage compressor through a higher-stage compressor, thereby getting a second and more volatile product — a "wilder" liquid — which was run back into the first tank and mixed with the first or heavier condensate. This mixture was then again weathered to a safe degree, whereby it lost the greater part of the more volatile product that had been condensed in the second stage.

Recently the process has been improved another step, in that the first stage compressor product is run into one tank and handled as ordinary gasoline; the second stage compressor product is run into a second tank and handled as a lighter gasoline,[1] with which the heavy refinery naphthas can be enriched or enlivened.

The last-mentioned method of using the second stage compressor product should receive wide recognition, and a market for the product should develop that would be no mean factor in the industry. Blending in the proportions of, say, 1 part of the product to 4 or 5 parts of the refinery naphthas makes these heavy naphthas more volatile and of greater value as fuel for automobiles; it also greatly increases their general usefulness.

Practical Deductions. — The natural gas of this country frequently contains light products that do not condense in the second-stage compressor, and for which it is practicable and necessary to install three, four, and even higher stage compressors. These light products — true gases at ordinary temperatures and pressures — can be compressed and liquefied, but the liquid gases so obtained must be handled as gases and not as oils. The mistake theretofore made in the "natural gas gasoline" industry, as some have recognized, has been the attempt to handle the light gaseous products as oils and not as gases.

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[1] Fithian, Dr. Edwin J., The fractionation of natural-gas gasoline, Natural Gas Association, sixth annual meeting, at Pittsburgh, Pa., May 16, 1911, Natural Gas Journal, August 1911, pp. 16–17.

CRUDE NATURAL GAS (*Ibid.*)

Constituents. — The natural gases of the Appalachian oil fields are not the complex mixtures generally reported, but are composed of the paraffin hydrocarbons with carbon dioxide and nitrogen as impurities. The gases that issue under considerable pressure or that are produced in quantities sufficient to justify piping for distant consumption consist principally of methane and ethane, the methane predominating. Small quantities of the higher paraffin hydrocarbons are also believed to be present. Olefin hydrocarbons and carbon monoxide have not been detected in the samples thus far examined,[1] and oxygen appears to be present only when the sample has been taken in a faulty manner and air has been admitted.

Natural gases that issue from old wells in which the original rock pressure has diminished contain higher members of the paraffin series, such as propane and butane, in larger quantities, and when a pressure below atmospheric is applied to the wells still larger quantities of the higher paraffins are obtainable. For example, in the oil pool surrounding Tidioute, Pa., a pool that has produced oil and gas for many years, the gas is now drawn from the wells under a pressure 12 to 13 pounds below that of the atmosphere, and a liquid product is obtained therefrom without the use of artificial pressure or cooling appliances.

Some natural gases in the United States contain methane only, and such gases are not adapted to the production of gasoline or liquid gas. Gases that contain no paraffin hydrocarbons higher than ethane require a pressure of 600 to 700 pounds to the square inch at 35° C. for the liquefaction of the ethane. At lower temperatures less pressure would be required. Since these high pressures are not used in the commercial plants producing gasoline from natural gas, ethane is not being liquefied in such plants, but a partial solution of the ethane in those paraffins that are liquefied undoubtedly takes place.

Propane and butane are on the dividing line between gases and liquids and must be handled as such — that is, as heavy gases or as very volatile liquids — and if held must be imprisoned in strong containers only. Pentane, hexane, and heptane are liquids under ordinary conditions and comprise ordinary gasoline.

Present Waste. — The vapors accompanying natural gas are clean and are ready for compression. They are analogous to the manufactured products, but have the great advantage over the latter of being ready made. However, they are at present in a great measure lost to the industries. The vapors should be compressed, as previously stated, but instead of being run into an open tank, or into a closed tank and weathered from it, with a corresponding loss, they should be run into steel containers and held there under compression.

Proposed Utilization of Products. — Some of the products of natural gas which are now going to waste could be compressed into containers and could be handled as gases. The process has been developed for other gas industries, but its promise as a profitable commercial enterprise in connection with the development of the new product has only recently been recognized.

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[1] By the Bureau of Mines.

The multiple-stage compressor may be used for obtaining a number of products or the single-stage compressor may be used for obtaining one product; then, by allowing this " wild " product to escape from a common container into a second, a third, and a fourth container, under partial pressures, it may be separated or fractionated into a second, a third, and a fourth product. This compression and later separation or fractionation of a common " wild " product into several products is, however, a waste of power, as ordinarily the gas should be compressed through several stages directly into its several products.

Yield of Liquid Product. — The following table gives the results of these experiments, in liquefying natural gas in which practically complete liquefaction was obtained:

Results of Compression and Cooling Tests of Natural Gas

Pressure exerted in liquefaction (pounds per square inch)	Temperature of cooling coil at entrance to storage tank	Volume of gas per gram of liquid
	° C.	c.c.
415	2.0	600.9
430	4.0	. . . . .
506	9.1	. . . . .
600	77.5	478.1

A pressure of 415 pounds at 2° C., of 430 pounds at 4° C., of 506 pounds at 9.1° C., or of 600 pounds at 77.5° C., liquefies practically the total volume of the gas being compressed. Assuming the liquid to be a mixture in which the propane and ethane predominate, as indicated below, 1 gram of liquid will yield 500 to 600 cubic centimeters of gas at 0° C. and 760 millimeters pressure; that is, 1 gallon of liquid will yield approximately 50 cubic feet of gas.

Properties of Crude Natural Gas and of the Volatilized Liquid Products. — The following table shows the composition of crude natural gas and of the volatilized liquid products of compression.

Analysis No. 1 is of the natural gas of Pennsylvania and West Virginia, which is used at Pittsburgh for heating and lighting purposes. This gas is not adapted to the production of gasoline, but the analysis is inserted here for comparison with the Follansbee gas, which was used in the production of gasoline.

Analysis No. 2 shows the composition of the crude natural gas from the wells at Follansbee before being subjected to compression at the commercial plant there.

Analysis No. 3 shows the composition of the gas left after the initial compression of 60 pounds to the square inch.

Analysis No. 4 shows the composition of the gas left after the final compression of 250 pounds to the square inch. This residual gas is turned into the mains for consumption in the ordinary manner. Its high quality is evident, it having almost twice the heating value of the natural gas used in Pittsburgh.

Properties of Crude Natural Gas and of the Volatilized Liquid Products of Compression

Analysis No.	Kind of gas	Specific gravity[1] (air = 1)	Heating value per cubic foot (0° C and 760 mm. pressure)	Composition				
				Methane	Ethane	Propane	Butane	Nitrogen
			B.T.U.	Per cent	Per cent	Per cent	Per cent	Per cent
1	Natural gas (Pa. and W. Va.)	0.64	1189	83 0	16.4	....	....	0 6
2	Natural gas (Follansbee, W. Va)	1 39	2468	..	21.8	77 7	....	0 5
3	Residual gas after 50-pound compression product has been removed	1 35	2364	. ..	34.9	64 6	....	0 5
4	Residual gas after 250-pound compression product has been removed	1 15	2008	... .	79 4	20 0		0 6
5		1 01	1808	3 8	95 0	.	..	1 2
6	Gas from liquefied gas (400	....	2066	.	72 5	27.0	... .	0 5
7	pounds pressure, 0° C)	1 28	2214		52 1	46 9	.	1 0
8		. .	2621	.	1 1	98 0		0 9
9		1 02	1816	4 7	94 9		.	0 4
10		..	1925	...	89 3	9 9	.	0 8
11	...do	..	2108	...	67 0	32 5	.	0 5
12		.	2161	. .	59 4	39 8	...	0 8
13			2708	. .	... .	89 2	9 9	0 9
14			3221	.	....	24 0	75 0	1.0

[1] By effusion method.

The four analyses next following, Nos. 5, 6, 7, and 8, show the composition of the liquid gas as obtained from the experimental plant erected by Allen and Burrell.

The next six analyses, Nos. 9, 10, 11, 12, 13, and 14, cover the analysis of the gas, from the first portion released to the last that came from the cylinder. The gas was taken from the top of the cylinder, and the first or more volatile portion approximated ethane in composition. The gases next volatilized contained less ethane and more propane, and, finally, in the last portion butane predominated. . .

Properties of the Paraffins Ordinarily Present in Natural Gas. — For comparison with the analyses described above, the properties of the paraffins ordinarily present in natural gas are given below:

Properties of the Paraffins Ordinarily Present in Natural Gas.

Name	Formula	Boiling point[1]	Specific gravity At different temperatures[2] (water = 1)	Specific gravity At 760 mm., and 0° C. (air = 1)[3]	Weight of 1 liter	Heating value per cubic foot, at 0° C. and 760 mm.[4]
		° C			Grams	B t u.
Methane .	CH_4	− 160	0 415 at − 160° C.	0 5529	0 7150	1065
Ethane ..	C_2H_6	− 93	.. . .	1 0366	1 3404	1861
Propane	C_3H_8	− 45 [5]	.. . .	1 5204	1 9659	2654
Butane	C_4H_{10}	1	... .	2 004	2 5914	3447
Pentane	C_5H_{12}	36 4	627 at 14° C.	......	......	4250
Hexane ..	C_6H_{14}	68 9	.658 at 20° C	.... .	......	5012
Heptane ..	C_7H_{16}	98 4	683 at 20° C	.... .	......	....

Name	Illuminating value	Liquefaction point	Other liquefaction points	Calculated volume of gas (at 60° F. and 30 inches pressure) from 1 gallon[6]	Theoretical volume of air necessary to burn 1 cubic foot of gas[6]
	British Candle-Power	° C. Pounds			Cubic feet
Methane	5 0 [7]	− 95 5 at 735 [8]	− 73 5° C at 835 lbs [9]	..	9 57
		− 81 8 at 807[10]	− 131° C at 98 4 lbs.[9]	..	.....
			− 12°C at 2700 lbs [11]	..	..
Ethane	35 0 [12]	+ 35 at 661[13]	Ordinary temp 690 lbs [14]	..	. ....
		+ 34 at 738[15]	− 4°C at 676 lbs [9]	53	16 75
Propane	53 9 [12]	+ 97 at 647[10]	. ...	45	23 92
Butane	.	. .	. . . .. .	37	31 10
Pentane	.		. . ..	31	38 28
Hexane	.		.. ..	27	.....

[1] Holleman, A. F., Organic chemistry, edited by A. J Walker, 1910, p. 41.

[2] Idem.

[3] Hempel, Walther, Methods of gas analysis. English translation, by L. M. Dennis, 1910, p. 482.

[4] Landolt and Börnstein, Physikalisch-chemische Tabellen, 3d edition, pp. 416, 425 (by J. Thomsen).

[5] Other authorities give − 17° C.

[6] Hunt, Charles, Gas lighting, vol. 3 of Chemical Technology, by C. E. Groves and Wm. Thorpe, 1904, p. 202.

[7] Wright, L. T., Jour. Chem. Soc. vol. 47, 1885, p. 200.

[8] Landolt and Börnstein, Physikalisch-chemische Tabellen, 1905, p. 185 (by Dewar).

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[12] Frankland, P., Jour. Chem. Soc. vol. 47, 1885, p. 235.

[13] Landolt and Börnstein, Physikalisch-chemische Tabellen, 1905, p. 182 (by Dewar).

[14] Idem, p. 182 (by Olszewski).

[15] Idem, p. 185 (by Olszewski).

CHARACTERISTICS OF LIQUEFIED NATURAL GAS (*Ibid.*)

The liquefied-gas product obtained from the third and fourth stage compressor product previously mentioned (but not the heavier first-stage compressor product, that which ordinarily remains after weathering) begins to boil at about – 40° C., and at its boiling point has a specific gravity of approximately 0.63. Its coefficient of expansion is estimated to be 0.0009 per 1° C. Its specific gravity at 15° C. would, therefore, be approximately 0.57 to 0.58.

When this liquid is confined the pressures generated by increasing the temperature are approximately as follows:

Pressures Generated by Heating Gasoline and Confined Liquefied Natural Gas

Tempera-ture	Refinery gasoline (80° B)	Natural gasoline obtained at —		
		50 pounds pressure	250 pounds pressure	400 pounds pressure
° C.	Pounds	Pounds	Pounds	Pounds
0	0	. .	107	360
5	0	9	117	375
10	0	12	130	398
15	0	16	144	423
20	3	20	154	453
25	5	25	175	482
30	10	30	193	510
35	16	34	210	545
40	26	40	231	585
45	41	46	251	630
50	92	52	275	690
55	350	58	. . .	755
60	. . .	65	. . .	. . .

From the above data the internal pressure generated by this volatile liquid, or the so-called " wild " product, is seen to reach 755 pounds per square inch at 55° C. This pressure is probably the maximum obtainable with the very light, or " wild," liquefied natural gas product having a specific gravity of 0.60 at 15° C., or 100° Bé. at 60° F. The fact that several gases, under pressures in excess of 150 atmospheres, or 2250 pounds per square inch, are successfully handled in commerce daily and have been so handled for a number of years, and the fact that this " wild " gas generates an internal pressure of only 755 pounds at 55° C.,

or 133° F., which would be an excessively high summer temperature, show that the ordinary handling of this liquefied gas in summer as well as in winter 'is simple and practicable, and can be done with appliances already developed and on the market. The margin of safety is ample.

It is important to note that many natural gases will not yield liquefied products by compression under ordinary commercial conditions, and the prospective investor is therefore cautioned to ascertain the nature of the vapor content of the gas under consideration before investing in an expensive compressor plant.

Power. — In order to determine the feasibility of using for power purposes the gas under discussion, a short test was made with a gas engine. A 10-horse-power two-cycle gas engine provided with a prony brake for absorbing the load, and equipped with the usual electric ignition, was used. The high-pressure cylinder containing the liquid gas was connected through a reducing valve to a small cylindrical receiver, capacity about 3 cubic feet, in which a pressure of about 3 inches of mercury was maintained; from this receiver a pipe connection led directly to the engine. No attempt was made to determine accurately the fuel consumption per horsepower-hour, nor to find the compression best adapted for the fuel, the test being made simply to determine the behavior of the gas in a commercial type of engine.

The test was of 30 minutes' duration; full load was easily maintained, and there was no difficulty whatever in keeping the engine up to speed. Throughout the test the engine ran easily, giving no indication of overload; there were no back fires nor preignitions. The indications were that the gas would make a satisfactory gas engine fuel. The brake horsepower (10.69) during the run was calculated from the following data:

Average revolutions per minute 277.7
Length of brake arm ....feet 5.25
Weight of brake arm .. . . .pounds 36.5
Total weight on scales . ...do 75
Effective weight on scales ....do 38.5

A cylinder of the liquefied gas was also used for driving a 30-horsepower automobile. A most satisfactory run was made for a number of miles, although no attempt was made to determine the efficiency developed, the only result desired being to demonstrate that the compressed product could be used for automobile propulsion. It was noted that the gas escaping from the container through the regulating valve supplying the engine became chilled and that considerable frost collected over the surface of the valve. This effect would, in general practice, soon freeze the liquid in the valve and clog the pipe entirely. By installing this valve near the engine exhaust the freezing may be prevented.

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THE COKE INDUSTRY IN 1919

Production Decreased but Capacity of By-product Ovens Increased

The outstanding features of the coke industry during the year 1919 were the great slump in demand that followed the armistice and a remarkable increase in the proportion of by-product coke made as compared with beehive coke. According to preliminary estimates made by F. G. Tryon, of the United States Geological Survey, Department of the Interior, the total production of coke in 1919, including beehive and by-product, but excluding gas-house coke, was 44,821,000 net tons, a decrease, as compared with 1918, of 11,657,000 tons, or 20.6 per cent. The decrease was confined almost entirely to beehive coke, the production of which fell off 36 per cent. The output of by-product coke decreased only 3.2 per cent. The output of by-product coke consequently exceeded that of beehive coke for the first time. In 1918 about 46 per cent of the total coke made in the United States was produced in by-product ovens and 54 per cent in beehive ovens. In 1919 the proportions were reversed, 56 per cent coming from by-product and only 44 per cent from beehive ovens. The year 1919 thus marked a turning point in the history of coke manufacture in the United States.

The quantity of coke manufactured in 1919 at illuminating-gas plants, not included in the figures given above, was about 3,200,000 tons. The total quantity of coke produced in 1919 was therefore about 48,000,000 tons.

These figures are preliminary only. Those for beehive coke are estimated from shipments by rail. Those for by-product coke are based on reports collected from producers in a preliminary canvass. The figures for both are subject to revision and will be revised when the annual statistical canvass is completed.

Beehive Coke

The blast furnaces are the great customers of the coke industry. In 1918, according to the statistical report of the American Iron and Steel Institute for 1918, they consumed 45,704,000 net tons of coke, or 81 per cent of the total output of beehive and by-product coke combined. In 1919 the production of pig iron fell off 22 per cent and

the demand for coke declined in proportion. The reaction was especially felt by the producers of beehive coke. With the growth in the output of by-product coke the beehive coke industry is likely to become more and more an auxiliary source of supply, carrying the peak load in times of extreme activity and correspondingly restricted in times of depression. This fact makes the current output of beehive coke a highly sensitive business barometer.

Table 1 shows in parallel columns the monthly output of pig iron and of beehive coke in 1919. The post-war slump in the demand for both began to be seriously felt about March 15. The low point for the year was reached in May. Thereafter production slowly recovered, only to be further interrupted by the steel workers' strike, which began September 22, and the coal strike of November 1 to December 10.

Table 1. — *Estimated Monthly Production of Beehive Coke and of Pig Iron in the United States in* 1919

Month	Beehive coke	Pig iron [1]
	(Net tons)	(Gross tons)
Monthly average, 1918	2,540,000	3,255,000
January...............................	2,384,000	3,306,000
February.........	1,787,000	2,948,000
March................................	2,091,000	3,088,000
April................................	1,343,000	2,474,000
May.................................	1,103,000	2,108,000
June.................................	1,148,000	2,114,000
July.................................	1,482,000	2,424,000
August	1,699,000	2,742,000
September............................	1,755,000	2,481,000
October.	1,521,000	1,864,000
November............................	1,647,000	2,407,000
December............................	1,690,000	2,630,000
	19,650,000	30,586,000

[1] Figures for 1918 quoted from American Iron Steel Institute; those for 1919 from Iron Trade Review.

As a result the production of beehive coke fell off 10,831,000 tons, or 36 per cent, from 1918 to 1919. The total output in 1919 is estimated at 19,650,000 net tons (Table 2). All districts shared in the decrease. The production in Pennsylvania and Ohio is placed at 14,861,000 tons, as compared with 22,276,000 tons the year before.

Table 2. — *Estimated Production of Beehive Coke, by Groups of States, in 1919, with Comparative Figures for 1918*

(*Net tons*)

	1918 [1]	1919 [2]
Pennsylvania and Ohio.................	22,276,000	14,861,000
West Virginia	2,717,000	1,061,000
Alabama, Tennessee, and Georgia........	2,042,000	1,695,000
Virginia and Kentucky, ...	1,535,000	1,201,000
Colorado, Oklahoma, and New Mexico	1,401,000	558,000
Washington and Utah	510,000	274,000
United States	30,481,000	19,650,000

[1] Final figures.   [2] Estimates.

By-product Coke

The total output of coke produced in by-product ovens in 1919 was 25,171,000 net tons, a decrease, as compared with 1918, of 827,000 tons, or 3.2 per cent. The effect of the decline in demand for by-product coke upon production was largely counteracted by the completion of new plants. The rate of production was higher during January, February, and March than during the remainder of the year.

Table 3. — *Rate of Production of By-product Coke per 30-Day Month in 1919*

	Net tons
First quarter..	2,260,000
Last three quarters	2,043,000
Year..................................	2,098,000

The dull season in the steel industry was most pronounced from April to July. During the last quarter of the year the by-product coke industry suffered from the combined effects of the steel strike, which restricted the demand, and of the coal strike, which curtailed the supply of coal.

The output by states is given in Table 4. The figures show a general increase as compared with 1918, which affected all states except New Jersey, Ohio, and Pennsylvania. The producers in Ohio reported an increase of 4 per cent. A larger increase (16 per cent) was made in New Jersey, and the largest of all in Pennsylvania, where the completion of new ovens caused an increase of 25 per cent.

In order of rank Pennsylvania came first, with 5,747,000 tons; Ohio second, with 5,445,000 tons; and Indiana third, with 3,691,000 tons. Pennsylvania has thus regained the first place as a producer of by-product coke, a position held by that state from 1915 to 1917 but lost to Ohio in 1918. Pennsylvania is now (1919) supreme in the coke industry. It is not only the largest producer of both beehive and by-product coke, but it supplies much of the coal consumed by by-product ovens in other states.

Table 4. — By-product Coke Produced in 1918 and 1919, by States,
with Increase or Decrease
(Net Tons)

State	1918		1919		Increase (+) or decrease (−)	
	Ovens	Tonnage produced	Ovens	Tonnage produced	Tons	Per cent
Alabama ...	847	2,634,451	906	2,255,000	− 380,000	− 14
Colorado.. ...	120	(a)	120	(a)	(a)	(a)
Illinois...	626	2,285,610	714	1,705,000	− 581,000	− 25
Indiana..........	1026	3,898,215	1216	3,691,000	− 207,000	− 5
Kentucky........	108	517,749	108	408,000	− 110,000	− 21
Maryland	180	474,368	360	356,000	− 118,000	− 25
Massachusetts ...	400	556,397	400	393,000	− 163,000	− 29
Michigan.. . . .	269	(a)	389	(a)	(a)	(a)
Minnesota.......	220	784,065	220	586,000	− 198,000	− 25
Missouri.........	56	(a)	56	(a)	(a)	(a)
New Jersey..... .	260	682,148	315	789,000	+ 107,000	+ 16
New York	615	1,069,587	591	751,000	− 319,000	− 30
Ohio...........	1658	5,226,334	1608	5,445,000	+ 219,000	+ 4
Pennsylvania. ..	2368	4,586,981	2846	5,747,000	+ 1,160,000	+ 25
Rhode Island.....	... .	....	40	(a)	(a)	(a)
Tennessee........	24	124,469	24	105,000	− 20,000	− 16
Washington	20	30,129	20	28,000	− 2,000	− 7
West Virginia.....	214	603,393	214	393,000	− 210,000	− 35
Wisconsin........	268	(a)	232	(a)	(a)	(a)
Combined States...	(b) .	2,523,684	....	2,519,000	− 5,000	− 0.2
Total........	9,279	25,997,580	10,379	25,171,000	− 827,000	− 3

(a) Included in combined States.
(b) Includes Colorado, Michigan, Missouri, Rhode Island, and Wisconsin, combined to avoid disclosing operations of individual companies.

By-product Ovens Completed in 1919

In 1919 a total of 1228 new by-product ovens were completed, of which 718 were new plants and 510 were extensions at existing plants. Pennsylvania put the largest number of new ovens in operation — 478. Indiana came second with 190, and Maryland third, with 180. One new state, Rhode Island, entered the ranks of by-product coke producers in January, when the Providence Gas Co.'s plant was completed.

Table 5. — *New By-product Ovens Completed and Put in Blast in* 1919

Company	Location of plant	Number of ovens	Type of ovens	Date blown in
New plants:				
International Harvester Co	South Chicago, Ill	88	Wilputte	Nov. 13, 1919
Steel & Tube Co of America	Indiana Harbor, Ind	120	Semet-Solvay	Aug. 28, 1919
Ford Motor Co	Detroit, Mich.	120	Semet-Solvay	Oct. 14 to Dec 6, 1919
Jones & Laughlin Steel Co	Pittsburgh, Pa.	210	Koppers	June 18, 1919
Rainey Wood Coke Co	Swedeland, Pa	110	Koppers	Aug. 26, 1919
Providence Gas Co	Providence, R. I.	40	Koppers	Jan. 28, 1919
Additions to existing plants:				
Tennessee Coal, Iron & R. R. Co	Fairfield, Ala.	77	Koppers	Dec. 17, 1919
Citizens Gas Co	Indianapolis, Ind	40	Wilputte	Jan. 31, 1919
Indiana Coke & Gas Co	Terre Haute, Ind	30	Koppers	Jan. 1, 1919
Bethlehem Steel Corp	Sparrows Point, Md	[1] 180	Koppers	Jan. 1, 1919
Seaboard By-Product Coke Co	Kearny, N. J.	55	Koppers	Jan. 21, 1919
Carnegie Steel Co..	Clairton, Pa.	128	Koppers	June 3 to July 1, 1919
Total		1228		

[1] Completed but not put in blast.

During the year 128 ovens were abandoned or were so rebuilt as to be classed as new ovens.

By-product Ovens under Construction January 1, 1920

Table 6 summarizes returns made to the United States Geological Survey from by-product operators on new ovens in construction at the beginning of 1920. In all 853 ovens are scheduled to come into operation by July 1, 1920. Of these ovens 247 are in Alabama, 220 in Pennsylvania, 210 in New York, and smaller numbers in Illinois, West Virginia, and Wisconsin. They are distributed among 11 projects, 6 of them new plants and 5 of them additions to existing plants.

Table 6. — *By-product Ovens under Construction January 1, 1920*

Operator	Location of plant	Number of ovens	Type of oven	Probable date of operation
Birmingham Coke & By-Products Co................................	Birmingham, Ala.	50	Koppers	Mar. 1, 1920
Sloss & Sheffield Steel & Iron Co....	Birmingham, Ala.	120	Semet-Solvay	May 1, 1920
Tennessee Coal, Iron & R. R. Co..	Fairfield, Ala.	77	Koppers	Feb. 1, 1920
St. Louis Coke & Chemical Co......	Granite City, Ill.	80	Roberts	June 1, 1920
Donner-Union Coke Corp.........	South Buffalo, N. Y.	150	Koppers	June 1, 1920
Lackawanna Steel Co............	Lackawanna, N. Y.	60	Semet-Solvay	July 1, 1920
Cambria Steel Co...............	Johnstown, Pa.	60	Cambria-Belgian	June, 1920
Jones & Laughlin Steel Co........	Pittsburgh, Pa.	60	Koppers	Apr. 1, 1920
Pittsburgh Crucible Steel Co......	Midland, Pa.	100	Koppers	June, 1920
Domestic Coke Corp.............	Fairmont, W. Va.	60	Koppers	May 1, 1920
Steel & Tube Co. of America	Mayville, Wis.	36	United-Otto	Jan. 1, 1920
Total.....................	....	853		

The completion of these projects will mean an increase of 8 per cent in the total number of by-product ovens in the country.   Construction is more active now than in the years immediately before 1914, when the European war began, but is less active than it was during the war. Much of the construction now under way was projected before the armistice.   The number of by-product ovens under construction in recent years has been as follows:

Table 7. — *By-product Ovens in Construction, 1914–1920*

January 1, 1914......	504	January 1, 1917....	2084
January 1, 1915......	644	January 1, 1918. .	2260
January 1, 1916......	1191	January 1, 1919....	1815
	January 1, 1920.....	853	

Types of Ovens

The following table shows the number of ovens of each type in existence on January 1, 1920, the number on January 1, 1919, and the number now under construction. Of the ovens put in operation in 1919, 860 were of the Koppers type; 240 were Semet-Solvay, and 128 were Wilputte.

Table 8. — Ovens in Use at Beginning and End of 1919, *and Building*
January 1, 1920
By Type

	In existence January 1, 1919	In existence January 1, 1920	Building January 1, 1920
Koppers	4829	5659	497
Semet-Solvay	2035	2275	180
United-Otto	1840	1754	36
Rothberg	281	257	...
Wilputte	78	206	...
Cambria-Belgian	90	90	60
Gas machinery	60	60	. : .
Klönne	42	42	...
Roberts	24	24	80
Piron	. .	12	. .
Total	9279	10,379	853

Plant Capacity for the Manufacture of By-product Coke

The capacity of a coke oven naturally depends upon the number of hours adopted as standard coking time. The maximum capacity of the by-product plants of the country, defined as " the maximum quantity of coke of the grade desired by the operator which can be produced when all conditions are favorable, with all ovens active," has been as follows:

Table 9. — Maximum Capacity of By-product Coke Ovens in the United States, 1918–1920, *in Net Tons per Annum*

January 1, 1918 27,000,000
January 1, 1919 33,700,000
January 1, 1920 39,500,000

In the year 1918 there was thus an increase in the annual capacity of coke ovens amounting to 6,700,000 tons, or 25 per cent. The increase during the year 1919 was somewhat smaller, 5,800,000 tons, or 17.2 per cent.

The annual capacity of the plants completed and in operation at the beginning of 1920, including ovens temporarily idle, was 39,500,000 net tons. This figure represents the output at full capacity — operation of 100 per cent. In actual practice an average operation above 90 per cent cannot be assumed for the country as a whole. Weekly reports received from the by-product plants during the war show that from

December 28, 1917, to February 1, 1919, the highest percentage attained for the entire country was 92.2, the output reached in the week ended September 28, 1918. The average for the year 1918, when every effort was being made to speed up the recovery of by-products, was 86.9 per cent of maximum capacity. The average for 1919 appears to have been about 70 per cent.

In estimating the coke or the by-products recoverable from the country's existing by-product ovens the assumed percentage of operation should therefore not exceed 90 per cent. Indeed, the safer figure ·of 85 per cent would appear better justified by experience. The present capacity of the by-product ovens of the country in net tons per annum would therefore be that shown in Table 10, the yield of coke from coal being taken as 71.2 per cent, the average for 1917–1918.

Table 10. — *Capacity of By-product Coke Ovens in* 1920

	Coke	Coal for charge
Assuming 90 per cent operation	35,500,000	49,800,000
Assuming 85 per cent operation	33,600,000	47,100,000

The completion of the plants now under construction may raise the capacity to a maximum of approximately 43,300,000 tons, or 36,800,000 tons under an operation of 85 per cent. In connection with the supposition that a limit to the production of by-product coke may be reached, it may be noted that this quantity is 65.2 per cent of the coke produced in 1918, the largest quantity ever used by the country in one year. It is 69 per cent of the coke required for producing 49,666,000 gross tons of pig iron, the annual capacity of the coke-burning blast furnaces completed or building on January 1, 1919, according to the . annual statistical report of the American Iron and Steel Institute, the · coke consumption being taken at 2375 pounds per gross ton of iron. It is 61.7 per cent of the country's total requirements for coke in the war year 1918, as estimated by the United States Fuel Administration, less sales of gas-house coke, amounting to 1,814,000 tons.

Recovery of By-products

The quantity and value of by-products recovered in 1919 may be approximated by multiplying the number of tons charged into the ovens in 1919 by the average quantity of by-products recovered in 1918 per ton.

Table 11. — *Average Recovery per Net Ton of Coal Charged into By-product Ovens in* 1918

NH_3 (all forms) expressed in terms of equivalent ammonium sulphate.. pounds	pounds	18.9
Tar	gallons	7.1
Crude light oil......................................	gallons	2.4
Gas..	M. cubic feet	10.4

The figures, if multiplied by the 35,353,000 net tons of coal charged in 1919, as estimated from known coke production on yield of 71.2 per cent, the average for 1917–1918, would give 668,200,000 pounds of ammonium sulphate or its equivalent, 251,000,000 gallons of tar, 84,800,000 gallons of crude light oil, and 367,700,000 cubic feet of gas.

For purposes of comparison the actual production of by-products in 1918 is reprinted below.

Table 12. — *By-products Obtained from Coke-oven Operations in* 1918

Product	Production	Sales	Value of sales
Tar (gal.)	263,299,470	200,233,002	$6,364,972
Ammonia:			
Sulphate (lbs.)	436,388,134	423,515,836	19,061,777
Liquor (gal.)	....	....	....
Anhydrous or free ammonia [1] (lbs.)	65,230,159	61,442,933	7,381,174
Gas:			
Illuminating and household purposes (M. cu. ft.)	385,035,154	33,437,991	7,130,113
Industrial purposes (M. cu. ft.)		124,920,488	6,569,402
Benzol products:			
Crude light oil (gal.)	87,222,450	3,764,272	963,043
Secondary light oil (gal.)	339,644	121,191	15,472
Benzol (gal.)	44,804,900	43,441,980	11,966,367
Toluol (gal.)	8,861,948	8,541,366	12,249,702
Solvent naphtha (gal.)	3,540,162	3,123,815	439,983
Other oils (gal.)...............	636,707	571,752	53,880
Crude naphthalene (lbs.)	10,614,799	10,403,758	287,581
Refined naphthalene (lbs.).......	5,472,699	5,486,689	362,648
Other products [2].................	....	....	1,756,345
Total	....	....	$74,602,458 [3]

[1] Includes liquor and sulphate sold by pound of NH_3.

[2] Includes sodium ferro cyanide, pyridin oil, nut coke, drip oil, spent oxide residue, coal-tar paint and wash oil.

[3] Does not include value of 1,999,370 net tons of coke breeze.

If the figures showing the recovery of by-products per ton are multiplied by the number of tons given above as the annual coke capacity of the ovens now built and building in the United States, namely, 36,800,000 tons — a moderate estimate assuming 85 per cent operation — the annual capacity for the recovery of by-products by the end of 1920 will become 977,100,000 pounds of ammonium sulphate, or its equivalent, 367,000,000 gallons of tar, 124,000,000 gallons of crude light oil, and 537,300,000,000 cubic feet of gas.

Hydrocarbons in Gasoline [1]

Name	Empirical formula	Structural formula	B. P.	Density
Paraffin hydrocarbons (C_nH_{2n+2}) Normal pentane	C_5H_{12}	$CH_3 - (CH_2)_3 - CH_3$	38° C.	$D\frac{0°}{4°} 0.6454$
Iso pentane	C_5H_{12}	$CH_3 - CH_2 - CH \big<^{CH_3}_{CH_3}$	28° C.	$D\frac{0°}{4°} 0.6393$
Normal hexane.........	C_6H_{14}	$CH_3 - (CH_2)_4 - CH_3$	69° C.	$D\frac{0°}{4°} 0.6770$
Iso hexane.............	C_6H_{14}	$CH_3 - (CH_2)_2 - CH \big<^{CH_3}_{CH_3}$	61° C.	$D\frac{0°}{4°} 0.6728$
Normal heptane........	C_7H_{16}	$CH_3 - (CH_2)_5 - CH_3$	98°.5 C.	$D\frac{0°}{4°} 0.7005$
Iso heptane	C_7H_{16}	$CH_3 - (CH_2)_3 - CH \big<^{CH_3}_{CH_3}$	90°.3 C.	$D\frac{0°}{4°} 0.6969$
Normal octane.........	C_8H_{18}	$CH_3 - (CH_2)_6 - CH_3$	125°.5 C.	$D\frac{20°}{20°} 0.7185$
Iso octane............	C_8H_{18}	$CH_3 - (CH_2)_4 - CH \big<^{CH_3}_{CH_3}$	119°.5 C.	$D\frac{20°}{20°} 0.7190$
Normal nonane	C_9H_{20}	$CH_3 - (CH_2)_7 - CH_3$	149°.5 C.	$D\frac{20°}{20°} 0.718$
Hydroaromatic hydrocarbons (C_nH_{2n}) (cycloparaffins or naphthenes) Cyclo-pentane-pentamethylene	C_5H_{10}	$CH_2 \big< ^{CH_2 - CH_2}_{CH_2 - CH_2}$	50°.5 C.	$D\frac{20}{4} 0.7506$
Methyl-cyclo-pentane Methyl-penta-methylene }	C_6H_{12}	$C_5H_9 - CH_3$	72° C.	$D\frac{21}{4} 0.7501$
Cyclo-hexane ... Hexa-methylene }... Hexa-hydro-benzene }...	C_6H_{12}	$CH_2 \big<^{CH_2 - CH_2}_{CH_2 - CH_2} \big> CH_2$	79° C.	$D\frac{0}{4} 0.7967$
Methyl-cycle-hexane Methyl-hexa-methylene } Hexa-hydro-toluene }	C_7H_{14}	$C_6H_{11} - CH_3$	94°-96° C.	$D\frac{0}{4} 0.780$
Aromatic hydrocarbons (C_nH_{2n-6}) .... Benzene................	C_6H_6	C_6H_6	80°.4 C.	$D_0 0.899$
Toluene...............	C_7H_8	$C_6H_5 - CH_3$	110°.3 C.	$D\frac{13}{4} 0.8708$
Xylene.................	C_8H_{10}	$C_6H_4 - (CH_3)_2$	142° C.	$D_0 0.8932$
Cumene	C_9H_{12}	$C_6H_5 - CH(CH_3)_2$	153° C.	$D_0 0.8798$

[1] Wilfred E. Guttentag (Petrol and Petroleum Spirits, pp. 54, 55).

A TABLE OF CONSTANTS FOR CERTAIN GASES AND VAPORS

All Volumes of Gases and Vapors are given at 60° F. and 30" pressure

The Temperature of Products of Combustion is reduced to 18° C. = 64.4° F.

I. NAME OF GAS OR VAPOR	II. FORMULA	III. Molec. Weight	IV. Sp. Gravity Gas or Vapor Air = 1.0	V. Boiling Point at 30" Fahr	VI. Sp Gravity Liquid Water=1.0 at 7"	VII. Sp. Heat Eq. Wt. of Coal Tar Water = 1.0	VIII. Cubic Feet per Pound	IX. Weight 1 Cubic Foot in Pounds	X. HEAT OF COMBUSTION Calories per kilo Grams	XI. Brit Therm Units Per Cu Ft	XI. Per Pound	XII. Per Cu Ft	XII. Per Pound	XIII. Air	XIV. Oxygen	XIV. CU FT PER CU FT OF COMBUSTIBLE CO₂	XV. H₂O	XVI. CO₂	XVI. H₂O	XVII.	XVIII. Air	XVIII. Reg. for Combust	XIX. POUNDS PER POUND OF COMBUSTIBLE Oxygen	XX. CO₂	XXI. H₂O	XXII.	XXIII. Size of Products at Comb. Temp.	XXIV. Calories per Kilo Grams	XXV. B.T.U. Per Cu Ft	XXV. Per Pound	XXVI. NAME OF GAS OR VAPOR
Carbon, to CO	C	24	0.8292				15.749	.06350	29,000	276 2	4,320		CO–2.0	4.785	1.0			1.121+	3.684+			CO–2.333+			+259 9	Carbon, to CO
Carbon, to CO₂	C	24	0.8292				13.749	.06350	96,960	923 5	14,344		1.0	9.570	2.0		2.666+	2.666+							+259 9	Carbon, to CO₂
Carbonic Oxide	CO	28	0.9671				13.503	.07407	67,900	333 5	4,368		0.5	2.393	0.5	1.0	1.871			+138 4				+1569 2	Carbonic Oxide
Hydrogen	H₂	2	0.0692		3.4090		186.620	.00530	66,300	326 2	61,523		0.5	2.393		1.0		9.000	34.624	8.000		9.000				Hydrogen
Methane	CH₄	16	0.5549	–13°	0.3929	0.4040	23.628	.04234	211,930	1009 0	23,838		1.0	9.570	2.0	1.0	2.0	2.250	17.312	4.000	2.750	2.250	+21,750	+103 1	+2935 6	+1713 6	Methane
Ethane	C₂H₆	30	1.0368	+33°			12.594	.07940	370,440	1764 4	22,255		2.0	16.748	3.5	3.0	3.0	1.900	16.156	3.733	2.933	1.900	+29,560	+136 0	+1713 6		Ethane
Propane	C₃H₈	44	1.5206	+100°	0.6273		8.387	.11643	529,210	2521 0	21,164		3.0	23.925	5.0	3.0	4.0	1.635	15.737	3.656	3.000	1.635	+35,110	+167 2	+1430 3		Propane
Butane	C₄H₁₀	58	2.0043	+33°			6.314	.15839	687,180	3274 0	21,236		4.0	31.103	6.5	4.0	5.0	1.552	15.520	3.596	3.004	1.552	+42,450	+202 2	+1317 3		Butane
Pentane	C₅H₁₂	72	2.9721	+106°	0.6640		5.248	.10055	847,110	4035 6	21,177		5.0	38.283	8.0	5.0	6.0	1.500	15.388	3.555	3.055	1.500	+47,850	+227 9	+1196 2		Pentane
Hexane	C₆H₁₄	86	2.9076				4.393	.22760	999,200	4768 0	20,914		6.0	45.458	9.5	6.0	7.0	1.463	15.293	3.534	3.069	1.463	+61,090	+290 9	+1175 4		Hexane
Ethylene	C₂H₄	28	0.9676		0.4040		13.493	.07410	333,330	1586 0	21,450		2.0	11.155	3.0	2.0	2.0	1.286	14.836	3.428	3.142	1.286	–2,710	–12 9	–174 2		Ethylene
Propylene	C₃H₆	42	1.4514				8.997	.11115	492,740	2347 2	21,120		3.0	21.533	4.5	3.0	3.0	1.286	14.836	3.428	3.142	1.286	+3,220	+15 3	+138 0		Propylene
Butylene	C₄H₈	56	1.9353	+23°			6.747	.14830	659,650	3099 2	20,913		4.0	29.710	6.0	4.0	4.0	1.286	14.836	3.428	3.142	1.286	+10,660	+50 7	+342 6		Butylene
Amylene	C₅H₁₀	70	2.4191	+102°		0.6311	5.398	.18525	807,630	3847 2	20,767		5.0	35.884	7.5	5.0	5.0	1.286	14.836	3.428	3.142	1.286	+18,970	+113 7	+614 1		Amylene
Acetylene	C₂H₂	26	0.8934				14.534	.06880	210,050	1451 7	21,465		2.0	11.963	2.5	2.0	1.0	0.92	13.313	3.07o	3.384	0.92	+47,770	–227 3	–3300 7		Acetylene
Allylene	C₃H₄	40	1.3823	+64°			9.447	.10555	467,540	2227 1	21,040		3.0	20.318	4.0	3.0	2.0	1.300	13.850	3.20o	3.259	1.300	–39,660	–186 8	–1784 2		Allylene
Crotonylene	C₄H₆	54	1.8661	+177°			6.998	.09480					4.0	20.00	5.5	4.0	3.0	1.300	14.1o5	3.259	3.349	1.300					Crotonylene
Benzene	C₆H₆	78	2.6953	+177°	0.8846		4.845	.20540	799,330	3807 5	18,447		6.0	35.838	7.5	6.0	3.0	0.692	13.313	3.076	3.384	0.692	–12,310	–17 3	–226 3		Benzene
Toluene	C₇H₈	92	3.179.	+230°	0.8720		4.107	.24345	855,630	4352 0	18,099		7.0	43.063	9.0	7.0	4.0	0.782	13.547	3.130	3.348	0.782	–3,320	–18 7	–68 8		Toluene
Xylene	C₈H₁₀	106	3.6630	+287°	0.8692		2.565	.29450					8.0	50.243	10.5	8.0	5.0	0.849	13.720	3.170	3.311	0.849					Xylene
Mesitylene	C₉H₁₂	120	4.1468	+328°			3.140	.17353					9.0	57.40	12.0	9.0	6.0	0.900	13.850	3.20o	3.300	0.900	+400	–2 3	+7 3		Mesitylene
Naphthalene	C₁₀H₈	128	4.4230	+424 4°	1.1517		2.952	.32870	1,283,310	6108 0	19,235		10.0	67.40	12.0	10.0	4.0	0.563	12.984	3.00o	3.427	0.563					Naphthalene
Hydrogen Sulphide	H₂S	34	1.1769		0.2433		11.056	.09012	140,900	672 2	7,459		1.5	3.349	1.5		1.0	0.929	SO₂–1.863	6.111	1.412			SO₂–1.883	+4,740	+22 6	+250 9	Hydrogen Sulphide
Ammonia	NH₃	17	0.5888		0.5683		22.178	.04400	90,630	428 8	9,598		0.75	3.490		1.5		1.988	N–0.823	6.111	1.412			N–0.823	+11,880	+56 7	+1259 0	Ammonia
Hydrocyanic Acid	HCN	27	0.9348				13.903	.07169	133,620	757 0	10,375		1.25	5.981			1.0	0.333	N–0.518	6.410	1.481	1.620	0.333	N–0.518	–27,460	–131 1	–1832 0	Hydrocyanic Acid
Cyanogen	C₂N₂	52	1.8000				7.248	.13779	250,620	1298 2	8,968		2.0	9.570			2.0		N–1.0	5.323	1.230	1.692			N–1.0	–65,700	–313 2	–2773 9	Cyanogen
Carbon Bi-Sulphide	CS₂	76	2.6296	+46°			4.96?	.20139	556,130	1914 6	6,270		3.0	14.355	3.0		1.0		SO₂–2.0	5.466	1.263	0.979			SO₂–2.0	–26,010	–124 0	–618 0	Carbon Bi-Sulphide
Methyl Alcohol	CH₃O	32	1.1121	141 2°	0.8027		11.·	.08910	182,750	873 9	10,250		1.5	7.178	1.5	1.0	2.0	1.125		6.492	1.500	1.375	1.125	+51,450	+246 4	+2994 0	Methyl Alcohol
Ethyl Alcohol	C₂H₆O	46	1.5894	172 9°	0.7946		.16	.12172	340,520	1623 0	13,235		3.0	14.355	3.0	2.0	3.0	1.174		9.033	2.087	1.913	1.174	+58,470	+278 5	+3298 0	Ethyl Alcohol
Carbonic Acid	CO₂	44	1.5196		0.2163		8.193	.11627																+463 1	+3379 1		Carbonic Acid
Water	H₂O	18	0.6217	+212°	1.0000		21.004	.04761																+371 1	+6670 4		Water
Sulphur Dioxide	SO₂	64	2.2128		0.155*		5.901	.16945																+357 3	+2937 3		Sulphur Dioxide
Oxygen	O₂	32	1.1052		0?.4		11.816	.08463																	+1999 1		Oxygen
Nitrogen	N₂	28	0.9701		0 438		13.040	.07429																			Nitrogen
Air			1.0000		.574		13.069	.07658																			Air

AUTHORITIES AND METHODS OF CALCULATION

In Column IX, the figures given ., Hempel's "Gas Anal.," p. 375, were selected for the fundamental v ght of Oxygen, Nitrog I, Hydrogen. Carbonic Oxide and Air.

The figures used for the con ... tion to English units m. ... , essures per liter at 0° C and 760 mm. X 0 ... = pounds per cu ft at 30" F and 30" pressure. The derivation of th .... actor employed.

$$\frac{.4922}{.4922} = \frac{.4a lb \times (.027.045 \times 30.00}{29.92 \times 520}) \quad .492}$$

The weights of the Compound Gases are ...culated from these data by Avogadro's law.

Column IV is calculated by the formula $sp gr = \frac{wt}{wt. 1 cu ft} \frac{1 cu. ft. gas, and}{air}$ and the figures thus obtained agree with the theoretical formula, $sp gr = \frac{2^{99}}{29}$

Columns V and VI are taken chiefly from Lunge's "Coal Tar and Ammonia"

Column VII. is from Ganot's "Physics," edition 1884; page 446.

Column X. and XXIII. are from Julius Thomsen's "Thermochemical Investigations," and the results are translated into English units in column XII. and XIII. and XXV.

Columns XIII and XVIII. are calculated on the assumption that air = 20.96 oxygen + 79 16 nitrogen by Volume
air = 23 156 oxygen + 76.876 nitrogen by Weight

Boiling points of benzene, toluene and xylene [1]

Benzene....................................... 80.4° C.[2]

Toluene....................................... 110.3° C.[3]

Xylenes....................................... 138° to 142° C.[4]

Specific Gravity Differences between Paraffin and Aromatic Hydrocarbons Having Approximately the Same Boiling Points

Paraffin Hydrocarbons

Hydrocarbon	B. P. °C.	Gravity
Dimethyl Pentane [5]	86°	0.711/0°
Diisobutyl [6] (b)	108°.5	0.713/0°
Nonane [7]	131°.5/751 mm.	0.742/12°.4
	135°–137°	0.732/12.7°

Aromatic Hydrocarbons

Benzene [8]	80.4	0.876/20°
Toluene [9]	110.3	0.871/14.7°
Xylene [10] (o)	142°	0.885/14.1°
(m)	139°	0.869/15.7°
(p)	138°	0.866/14.7°

[1] Rittman, Twomey and Egloff, Met. and Chem. Eng. 1915, 682.

[2] Kuops, Leibig Ann. 248, 175 (1888).

[3] Landolt and Jahn, Z. Phys. Chem. 10, 303 (1902).

[4] Barbier and Rowe, Bull. soc. chim. 3255 (1890); Weegman, Z. Phys. Chem. 2237 (1888).

[5] Ladenburg, Liebig Ann. 142, 310, (1867.)

[6] Kopp, Liebig Ann. 95, 336, (1855.)

[7] Lemoine, Bull. Soc. Chim., 41, (164.)

[8] Kuops, Liebig Ann. 248, 175, (1888.)

[9] Landolt and Jahn, Z. Phys. Chem. 10, 303, (1892.)

[10] Barbier and Rowe, Bull. Soc. Chim. 3255, 1890; Weegman, Z. Phys. Chem. 2237, 1888.

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